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I hereby recommend that the thesis prepared under my supervision by ___ CPT Steven Oluic' ___

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The Photocatalytic Destruction of Volatile

Organic Compounds in Water

be accepted as fulfilling this part of the requirements for the degree of ___ Master of Science ___

Approved by:

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THE PHOTOCATALYTIC DESTRUCTION OF VOLATILE ORGANIC
COMPOUNDS IN WATER

.A thesis submitted to the

Division of Graduate Studies and Research
of the University of Cincinnati

in partial fulfillment of the
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MASTER OF SCIENCE

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by

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B.A., Case Western Reserve University, 1983

Abstract

Ground water at the Anniston Army Depot in Anniston, Alabama has been found to be contaminated with volatile organic compounds. Recent research has indicated that advanced oxidation processes, namely hydrogen peroxide catalyzed by ultraviolet light radiation, can be successful in destroying these contaminants. In this process hydrogen peroxide is decomposed by ultraviolet radiation producing hydroxyl free radicals which in turn oxidize the organic compounds present.

A series of batch tests and flow-through experiments using this oxidation process was performed on a synthetic wastewater that closely duplicated contaminant concentration levels found at Anniston. These contaminants, 1,2 dichloroethene, trichloroethene, dichloromethane and benzene, were found readily destructed by the UV/H_2O_2 process both individually and in mixtures during batch testing and in flow-through experiments. All experimentation was performed utilizing a thin film reactor.

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Acknowledgement

There are many people important to me to whom I could thank for their assistance and support during my assignment at the University of Cincinnati in the preparation and successful completion of my Master of Science degree.

I owe a tremendous debt of gratitude to COL Bruce K. Scott for his confidence in me as an officer and for opening the door for me to the U.S. Army's Advanced Civil Schooling Program. To the officers and men of Bravo Company, 16th Engineer Battalion, especially 1SG Clyde Hills and SFC Arthur Perez, who served under my command and whose marvelous performance as combat engineers were reflected on my evaluation reports. It was these reports that resulted in my being chosen to attend graduate school.

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1 Introduction

The presence of volatile organic compounds (VOCs) in
groundwater at United States military installations throughout
the world has presented the U.S. military with challenges in
installation remediation. The majority of this remediation
work is presently done using packed bed aeration or granular
activated carbon (GAC) to remove the VOCs from the
groundwater. There are problems associated with using these
methods. Packed bed aeration does not remove all contaminants,
or does so very inefficiently, therefore, with stricter
regulations for air quality, this process may not be allowed
at all in some instances. Using GAC has been proven to be very
effective in the recent past. However, once the adsorptive
capacity of the GAC is reached, it either has to be
regenerated or disposed as a waste. Then the problem of high
cost becomes important. The cost of disposing the contaminated
GAC in a secure landfill is very high. Additionally, GAC is
inefficient when treating water of low level contaminant
concentration.

Recent studies in advanced oxidation processes have shown
that hydrogen peroxide (H_2O_2) catalyzed by ultraviolet light
(UV) will destroy VOCs (Sundstrom, 1991). The advantage in
this treatment method lies in the fact that the VOCs are
destroyed and not simply removed or transferred into another
phase. UV light accelerates the rate of removal of a VOC by

activating the H_2O_2, which splits into two hydroxyl radicals. These hydroxyl radicals attack the organic molecules by abstracting hydrogen atoms or by adding to double bonds.

The UV/hydrogen peroxide process has been proven effective in the treatment of TNT-containing wastewaters and for the removal of various VOCs from groundwater and the removal of various contaminants from industrial wastewater (Pinto,1991). The treatment of VOC contaminated groundwater must be site specific, requiring evaluation of the groundwater in the lab prior to the UV/hydrogen peroxide process use.

The majority of studies done on the hydrogen peroxide catalyzed by UV process have been performed on pure compounds. A recent study by Sundstrom (1990) indicated that the rate of VOC destruction is significantly affected by the number of VOCs present. The competing reactions during VOC destruction slows down the destruction rate. Most studies have either been done with batch or annular reactors using this process. However, flow through systems have been developed and are currently being used, but the majority of this information is proprietary and thus not available in the open literature.

This research explored the utility of using the UV/H_2O_2 oxidation process on VOC contaminated water in a flow through system which uses a thin film reactor. Information on contamination levels in groundwater found at the Anniston Army Depot was used in the preparation of the synthetic wastewater. Concentration levels can be found in Table 2.5.

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2 Literature Review

2.1 Theoretical Background

Photolysis (or photodegradation) is a process that breaks down a chemical or compound by light energy, usually in a specific wavelength range (EPA 540/2-90,1990). The ability of UV light to destroy organics alone is sometimes negligible.

Photocatalysis is an advanced oxidation process that uses the combination of UV radiation and an oxidant, in this case hydrogen peroxide (H_2O_2) to create a stronger oxidant, OH·, to destroy organic contaminants. This process, when carried through to completion, converts hydrocarbons and various other organics to carbon dioxide and water. Halogens present are converted to the corresponding inorganic halide ions (Bernardin, 1990).

2.2 UV Radiation

UV radiation, or light, can be defined as electromagnetic radiation having wavelengths shorter than visible light but longer than X-ray radiation (Legan, 1982). In this research the spectrum of interest was between 180 nm and 380 nm. Figure 2.1 displays the spectrum of electromagnetic radiation. The lamp used was a low pressure, 25 Watt, General Electric germicidal lamp tube. Low pressure lamps are the most efficient source of UV energy (Pinto, 1991). The light emitted is nothing more than a stream of photons carrying energy. The following equation governs the amount of energy carried by a

photon:

$$E = h\nu = hc/\lambda \qquad (1)$$

E = specific energy
h = Planck's constant
ν = frequency
c = speed of light
λ = wavelength

It can be seen that a photon's energy is determined by the transmitted light's wavelength.
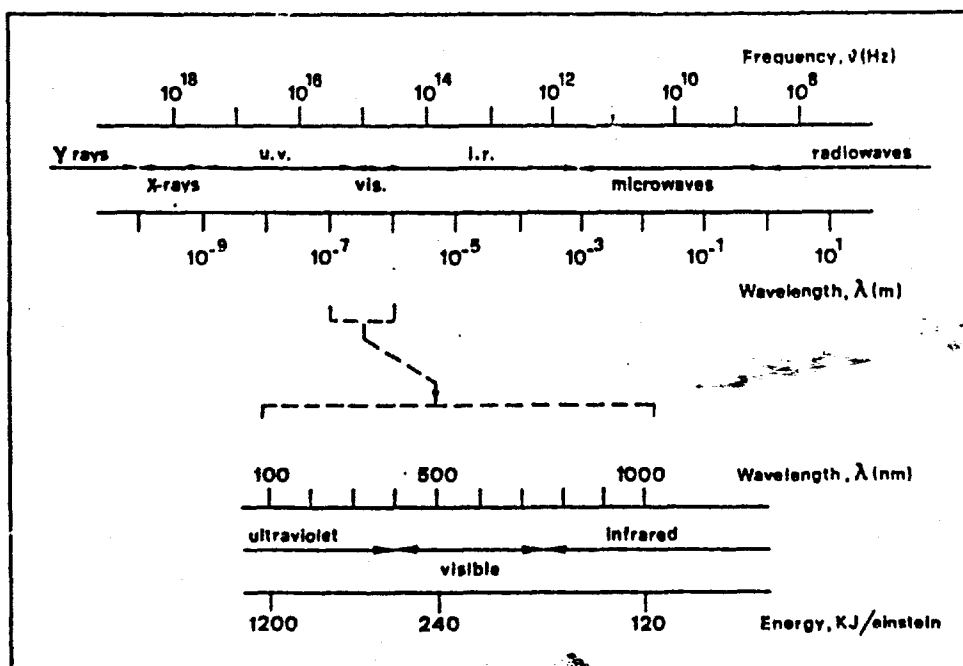
Figure 2.1 Spectrum of Electromagnetic Radiation
(Photocatalysis, 1989)

Atoms and molecules absorb only those wavelengths that provide the necessary energy to alter their state through

either a physical or chemical change. UV light will typically cause a transition of electrons from one orbital to another and if the electron belongs to a chemical bond, the bond may be broken (Legan, 1982). Table 2.1 lists the dissociation energies for chemical bonds.

Another crucial factor in UV radiation and its impact in photocatalysis is intensity. An increase in intensity results in an increase of energy or, photons of UV light being delivered. This is expressed in the following equation:

$$E = I \ T \qquad (2)$$

I = intensity
E = UV dose
t = contact time

2.3 UV & Hydrogen Peroxide

Ultraviolet light in combination with hydrogen peroxide is coming to the forefront as an advanced oxidation process for use in environmental applications. When H_2O_2 is catalyzed with UV light hydroxyl radicals are formed. The wavelength emitted by the UV lamp provides the correct amount of energy required to break the H_2O_2 molecule into hydroxyl radicals. Table 2.2 shows some examples of typical photochemical reactions. The hydroxyl radicals formed are very powerful oxidants which will react to destruct organic contaminants. Table 2.3 lists oxidation potentials for some common oxidants. It can be seen that the hydroxyl radical is only second to the fluorine ion in oxidation potential.

Table 2.1   Dissociation Energies for Various Chemical Bonds

| Bond | Dissociation energy kcal/gmol | Maximum wavelength to break bond, nm | If absorbed will this light break the bond? | |
			253.7	184.9
Carbon				
C - C	82.6	346.1	yes	yes
C ≡ C	199.6	143.2	no	no
C - Cl	81.0	353.0	yes	yes
C - F	116.0	246.5	no	yes
C - H	98.7	289.7	yes	yes
C - N	72.8	392.7	yes	yes
C = N	147.0	194.5	no	yes
C ≡ N	212.6	134.5	no	no
C - O	85.5	334.4	yes	yes
C = O (aldehyde)	176.0	162.4	no	no
C = O (ketone)	179.0	159.7	no	no
C - S	65.0	439.9	yes	yes
C = S	166.0	172.2	no	no
Hydrogen				
H - H	104.2	274.4	yes	yes
Nitrogen				
N - N	52.0	549.8	yes	yes
N = N	60.0	476.5	yes	yes
N ≡ N	226.0	126.6	no	no
N - H (NH)	85.0	336.4	yes	yes
N - H (NH$_3$)	102.0	280.3	yes	yes
N - O	48.0	595.6	yes	yes
N = O	162.0	176.5	no	no
Oxygen				
O - O (O$_2$)	119.1	240.1	no	yes
- O - O -	47.0	608.3	yes	yes
O - H (water)	117.5	243.3	no	yes
Sulfur				
S - H	83.0	344.5	yes	yes
S - N	115.0	248.6	no	yes
S - O	119.0	240.3	no	yes

Source: Legan, 1982.

Table 2.2 Examples of Photochemical Reactions and
their Effects (Legan, 1982).

Reaction	Effective Wavelength, nm	Result
$H_2O + h\nu = H\cdot + HO\cdot$	184.9	Water broken into free radicals.
$H_2O_2 + h\nu = 2\ HO\cdot$	253.7	Hydrogen Peroxide broken into free radicals.
$O_2 + h\nu = O_3$	253.7	Oxygen molecules broken converted to ozone.
$RH + h\nu = H\cdot + R\cdot$	184.9	Organic broken into free radicals.
$Fe^{+2} + h\nu = Fe^{+3}$	253.7	Ferrous iron converted to ferric ion.
$NO + h\nu = N_2 + O_2$	184.9	Nitric oxide decomposed.
$NH_3 + h\nu = NH2\cdot + H\cdot$	184.9	Ammonia broken into free radicals.

Table 2.3 Oxidation Potential of Oxidants
(Bernardin, 1991)

Relative Oxidation Power, Chlorine = 1	Species	Oxidative Potential (volts)
2.23	Fluorine	3.03
2.06	Hydroxyl Radical	2.80
1.78	Atomic Oxygen (singlet)	2.42
1.52	Ozone	2.07
1.31	Hydrogen Peroxide	1.78
1.25	Perhydroxyl Radical	1.70
1.24	Permanganate	1.68
1.17	Hypochlorous Acid	1.59
1.15	Chlorine Dioxide	1.57
1.07	Hypoiodous Acid	1.45
1.00	Chlorine	1.36
0.80	Bromine	1.09
0.39	Iodine	0.54

Studies by Borup (1987) indicate that the following chain of reactions take place in a H_2O_2/water system in the presence of UV radiation:

$$H_2O_2 \xrightarrow{uv} 2\ OH\cdot \qquad\qquad (3)$$

$$H_2O_2 + OH\cdot \longrightarrow H_2O + HO_2\cdot \qquad\qquad (4)$$

$$HO_2\cdot + H_2O_2\cdot \longrightarrow H_2O + O_2 + OH\cdot \qquad\qquad (5)$$

$$2HO_2\cdot \longrightarrow H_2O_2 + O_2\cdot \qquad\qquad (6)$$

The net result is:

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad\qquad (7)$$
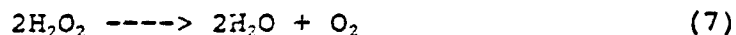
When hydroxyl radicals are formed under photocatalysis in the presence of target compounds, many more reactions may take place than those shown. The formation of intermediate products may occur in which the hydroxyl radicals will also be involved in their own destruction, as well as destruction of the compounds of interest. These competing reactions may adversely effect the overall reaction rates and destruction.

Several variables effect the UV/H_2O_2 process. These variables are listed in Table 2.4.

Table 2.4 UV/H_2O_2 Process Variables
```
------------------------------------------
        1. Ultraviolet light dosage
        2. Hydrogen peroxide dosage
        3. pH conditions
        4. Temperature conditions
------------------------------------------
```

Studies by Weir (1987), Sundstrom (1990), and Bernardin (1990) indicate that the intensity of the UV radiation in a UV/H_2O_2 process significantly effects the rate of destruction.

Figure 2.2 and Figure 2.3 clearly illustrate the effects of UV radiation intensity on the rates of destruction for benzene and trichloroethylene. As the light intensity increases, the compounds are oxidized more rapidly since more UV photons are being supplied to the reaction mixture per unit time. Current proprietary UV/H_2O_2 systems utilize high intensity UV lamps. Froelich (1991) indicated that a broader range of organic molecules can be activated due to the broad spectrum UV output with high intensity lamps.

As with UV light intensity, increasing the initial H_2O_2 concentration also produces enhanced rates of reaction/ destruction due to the increased supply of hydroxyl radicals. Sundstrom (1990), Weir (1987) and Borup (1987) indicated that an increase in initial H_2O_2 concentration resulted in increased rates of organics destruction. However, Mansour (1985) and Froelich (1991) indicate that a UV/H_2O_2 system could be overdosed with H_2O_2 which would slow down the reaction rates. This is attributed to excess H_2O_2 which absorbs the UV light energy inhibiting the UV activation of the organic contaminants and resulting in slower destruction rates

Temperature and pH have been observed to somewhat effect the performance of UV/H_2O_2 systems. Sundstrom (1986) noted some effects of temperature increasing the reaction rates. However, this was to the use of high intensity lamps which caused high temperatures in the solution being treated. The higher temperature coincided with the increased production of
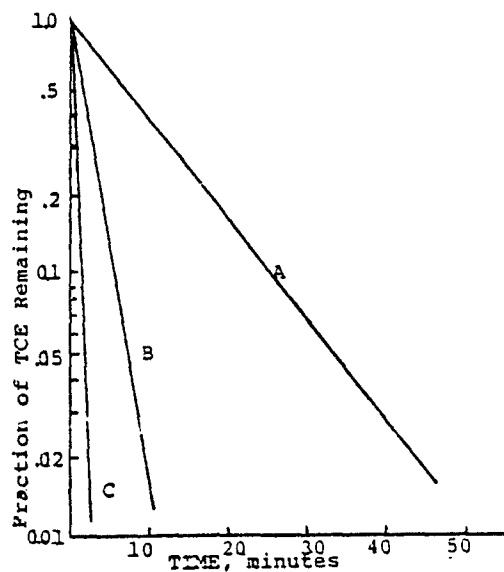
Line A - Data from Sundstrom, 2.5 W/liter
Line B - Data from Hager at 230 W/liter
Line C - Data from Proprietary Equip. 500 W/liter

Figure 2.2 Effect of UV Intensity on Destruction Rate
(Bernardin, 1991).
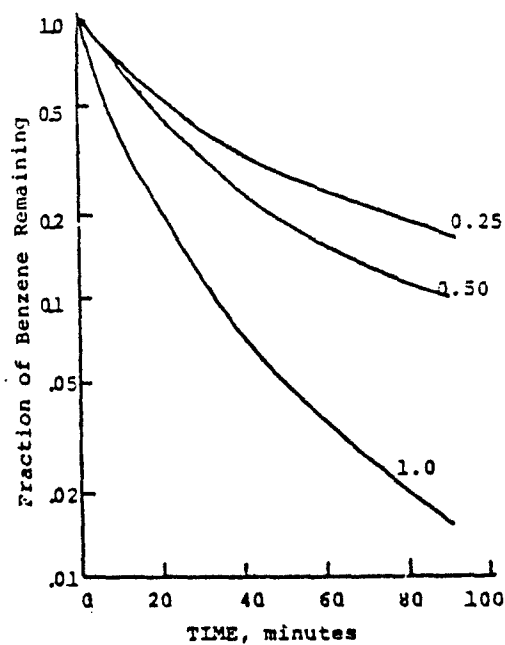
Figure 2.3 Effect of Relative UV Light Intensity on the
Decomposition of Benzene (Weir, 1987).

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hydroxyl radicals when using high intensity lamps. Overall, temperature has demonstrated a negligible effect on the rate of photochemical reactions using low pressure lamps (Pinto, 1991).

Several studies have shown that pH does effect the UV/H_2O_2 oxidation process. Mansour (1985) and Sundstrom (1986) observed the rate of reaction increasing with increasing pH.
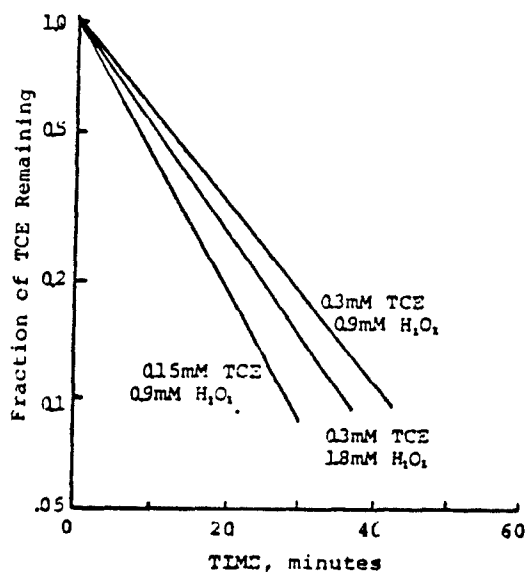
Figure 2.4 Effect of Initial Benzene and Hydrogen Peroxide Concentrations on Benzene Destruction (Sundstrom, 1990).

The range of pH in their experimentation was from 2 to 9. On the other hand, Weir (1987) observed a slower rate of destruction of benzene in an alkaline setting. It was

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determined that at pH 10.5 the H_2O_2 quickly degraded under these conditions in which perhydroxyl ions ($HO_2\cdot$) would consumed the H_2O_2, resulting in a net loss of hydroxyl radical production. The indication here is that under excessive alkaline conditions there is inhibition of oxidation.

2.4 Organic Chemicals

The Volatile Organic Compounds (VOCs) used for the experiments in this thesis were representative of those found present in groundwater at the U.S. Army Anniston Depot. Table 2.5 lists these chemicals and their average concentrations.

Table 2.5 Average VOC Concentrations in Groundwater at the Anniston Army Depot

1,2 dichloroethylene	7368 ug/L
trichloroethylene	2970 ug/L
methylene chloride	480 ug/L
benzene	110 ug/L

1,2 dichloroethene (1,2 DCE)

$$ClHC = CHCl$$

1,2 DCE is also known as 1,2 dichloroetylene or acetylene dichloride. Its primary use is as a solvent for fats, phenol, and camphor. On military bases it is used as a solvent, primarily in heavy maintenance or machining operations. 1,2 DCE is found in either a cis- or trans- form. Pertinent data

for 1,2 DCE follows:

Table 2.6 Chemical Properties of 1,2 DCE

Formula Weight	96.95
cis- boiling pt.	59.6°C
melting pt.	-81.5°C
trans- boiling pt.	47.2°C
melting pt.	-49.4°C
density at 25°C	1.4435
water solubility	600 mg/L

Trichloroethene (TCE)

$$ClHC = CCl_2$$

TCE is also known as trichloroethylene or ethinyl trichloride. Its primary use is as a solvent for fats, waxes, resins, oils, rubber, paints, and varnishes. It is used as a universal degreaser, in drycleaning, and in the manufacture of organic chemicals. On military bases it is used as a universal degreaser/solvent. The chemical data for TCE are shown in Table 2.7.

Table 2.7 Chemical Properties of TCE

Formula Weight	131.39
boiling pt.	86.7°C
melting pt.	-84.8°C
density at 25°C	1.456
water solubility	1100 mg/L

Dichloromethane

$$CH_2Cl_2$$
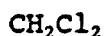
Dichloromethane is commonly referred to as methylene chloride or methylene dichloride. Its primary use is in degreasing and cleaning fluids and as a solvent in food preparation. On military bases it is used in much the same manner as 1,2 DCE or TCE. Pertinent data for dichloromethane is shown in Table 2.8.

Table 2.8   Chemical Properties of Dichloromethane

Formula Weight	84.93
boiling pt.	39.75°C
melting pt.	95°C
density at 25°C	1.316
water solubility	20,000 mg/L

Benzene

$$C_6H_6$$

Benzene is also referred to as benzol, although this is uncommon. It is primarily used in the manufacture of medicinal chemicals, dyes and many other organic compounds, artificial leather, linoleum, oil cloth, airplane dopes, varnishes and lacquers. It is occasionally used as a solvent for waxes, resins and oils. On military bases it is primarily associated with contamination due to degreasing/solvent use and fuel storage and spillage. Table 2.9 lists pertinent chemical data.

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Table 2.9   Chemical Properties of Benzene

        Formula Weight   78.11
        boiling pt.   80.1°C
        melting pt.   5.5°C
        density at 20°C   1.501
        soluble in water at 23.5°C
----

3   Materials and Methods

3.1 Apparatus & Chemicals

Ultraviolet Lamp

Throughout the course of experimentation only one type of lamp was used as the UV light source. A General Electric low pressure germicidal lamp, Model G25T8, with a nominal power rating of 25 watts (W) was used in the quartz glass thin film reactor. Once inserted in the reactor the combination was placed in a standard fluorescent light fixture. Ninety per cent of the light emitted is in the 254 nm wavelength range.

A UVX Digital Radiometer was used to measure UV light intensity along the length of the UV lamp tube. This was done with the lamp alone, inserted in a quartz glass sleeve, and the reactor so as to determine the actual UV light intensity in the solution passing through the reactor. Table 3.1 lists the intensities with and without the quartz sleeve and the reactor along the lamp's length. Figure 3.1 displays the UV intensity along the length of the UV light tube.

The loss of intensity through one layer of quartz glass was approximately two uW/cm^2 across the length of the UV lamp tube. The actual intensity which reacted with the compounds in solution in the thin film reactor was on the order of eight to ten uW/cm^2.

Quartz Thin Film Reactor

The quartz thin film reactor was specially fabricated for

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Table 3.1 Intensity along 25 W UV Light Tube

Point in inches	Intensity in uW/cm^2		
	w/o quartz sleeve	w/ quartz sleeve	with reactor
0.5	2.31		
1.0	11.48	8.01	1.79
2.0	10.10	7.93	2.98
3.0	12.10	9.73	3.00
4.0	12.28	10.10	3.05
5.0	12.20	9.78	3.12
6.0	12.20	10.27	3.08
7.0	12.28	10.39	3.01
8.0	12.31	10.40	3.04
8.438	12.48	9.96	3.08
9.438	12.44	9.90	3.17
10.438	12.37	10.03	3.15
11.438	12.39	10.18	3.14
12.438	12.36	10.20	3.10
13.438	12.24	9.27	3.12
14.438	9.40	8.75	2.78
15.438	8.02	8.26	1.95
15.938	1.82		

Fig. 3.1   UV Lamp Intensity

Legend: —■— w/o quartz sleeve   —+— w/ quartz sleeve   —*— w/ reactor

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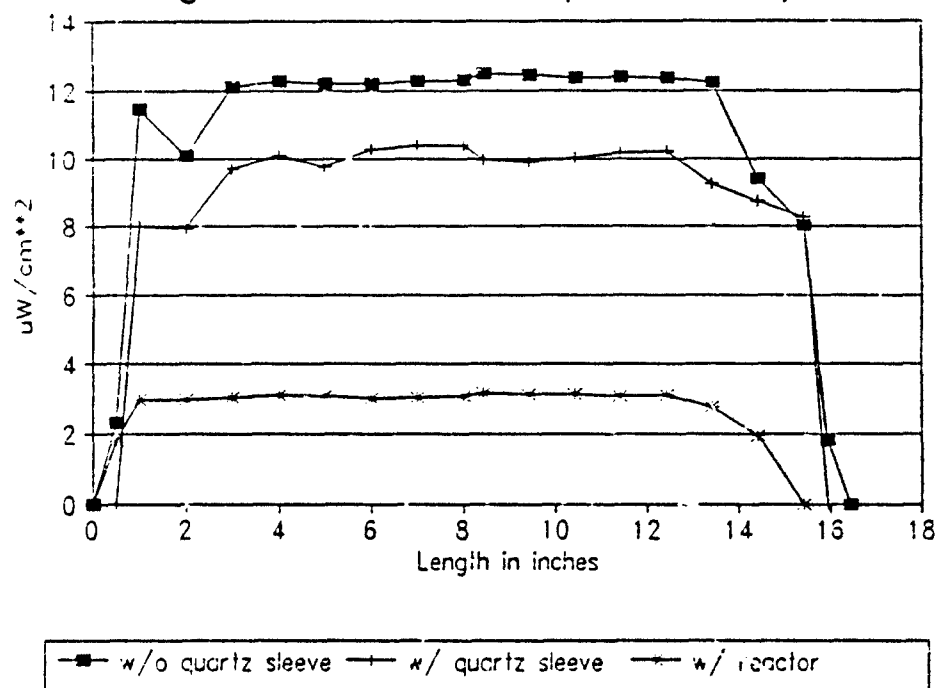
the Department of Civil & Environmental Engineering at the University of Cincinnati. The reactor is pictured in Figure 3.2 . Other pertinent data is listed in Table 3.2.

Table 3.2 Thin Film Reactor Specifications

Overall Length	40.75 cm
Inside diameter	2.70 cm
Outside diameter	3.50 cm
Reactor Volume	96.0 ml
Thin film width	0.3 cm
Manufacturer: Paxton Woods Glass	

Exit or entrance ports are located at opposite ends on opposite sides of the reactor.

Flow-through System and Operation

The flow-through system is pictured in Figure 3.2 . All fixtures and equipment were either glass, teflon, or stainless steel. To make the system operational, two modified glass two liter graduated cylinders were used. Each were identical in that they had an exit port located at the bottom and a teflon "float" which fit inside the cylinder. The floats provided zero headspace in the cylinders which minimized any VOC loss through volatilization out of the solutions. Teflon tubing was used throughout the setup. The tubing was formed by gently heating it with a Bunsen burner and slowly bending the tubing as it became malleable and holding it in the desired position for several seconds. A Fluorocarbon, Model SPM 100, Teflon pump was used with a Cole Parmer, Model No. 2630, Power Supply. Voltage used throughout was 110 D.C.. All stainless
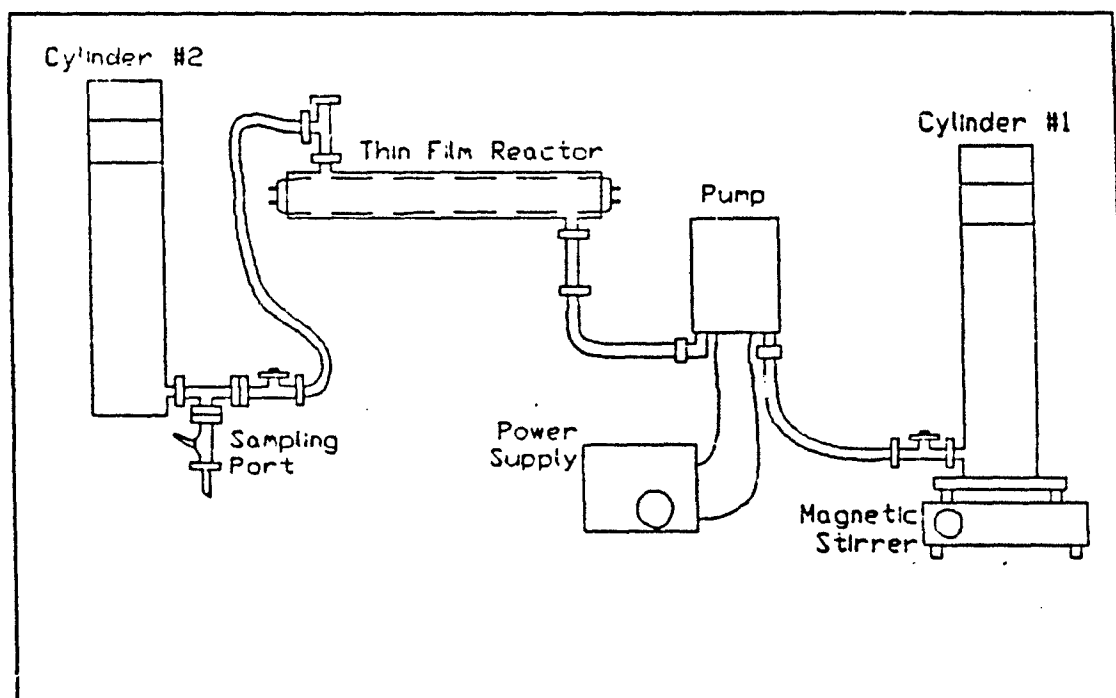
Figure 3.2   Flow-through Reactor Setup

steel fittings and the sampling valve were made by Swagelok. The teflon valves used on the graduated cylinders were purchased from Cole Parmer.

Cylinder 1, which initially contained the synthetic wastewater to be pumped through the system, was placed on an asbestos pad which sat on top of a magnetic stir plate. A stir bar was previously placed in the cylinder.

Three flow-through experiments were performed using this setup. To simulate the continuous flow, the solution was pumped through the thin film reactor while the UV light was on. Once cylinder 2 was full the teflon valve on the cylinder was closed and the UV light and pump switched off. Cylinder 1 was not entirely emptied, enough of the solution remained to keep the head space free system intact. Next, the polarity on the power source was switched to allow for pumping in the opposite direction and the process repeated. Throughout the experiments the thin film reactor was covered with aluminum foil to reflect UV light back into the solution and to provide some degree of protection from the harmful effects of UV radiation. The power supply selector dial was set at the six position which maintained a consistent flow rate in both directions.

Each experiment had slightly different flow rates. Table 3.3 lists the rates. Turning the power selector knob to the value six in each of the three experiments was slightly different. This helps to account for the difference in flow

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rates among the flow through experiments.

Table 3.3   Flow-through Flow Rates
```
------------------------------------
    Experiment 1        309.9 ml/min.
    Experiment 2        370.3 ml/min.
    Experiment 3        422.6 ml.min.
------------------------------------
```

Samples were drawn at predetermined intervals through a sampling valve located at Cylinder 2. Headspace-free, teflon capped 15 ml vials were used to store the samples. Two samples were taken at each sampling time. All samples were stored in a container box at room temperature until analyzed using the GC/MS.

The batch experiments were performed in the same apparatus, however, instead of using the flow-through method the solution remained exposed to UV light in the reactor for each specified length of time. When the time limit was reached, the UV light was switched off and as the reactor was emptied for the untreated solution to be pumped in, two samples were taken using the same method and vials as in the flow-through experiments.

Upon completion of a set of experiments with the quartz thin film reactor, four liters of laboratory grade (Millipore Super Q) water was pumped through the system to flush any trace contaminants out. The modified graduated cylinders were placed in the glassware oven at 250°C for a minimum of two hours. New vials were used for all sample aloquots.

Organic Chemicals

1,2 dichloroethene (1,2 DCE), trichloroethene (TCE), dichloromethane, and benzene were used in the synthetic wastewater solution's preparation. Predetermined amounts of each chemical were injected into 1670 ml of Super Q water in one of the modified graduated cylinders, which contained a clean magnetic stir bar. Each chemical was quickly injected into the water using a 25 or 10 ul syringe and then the teflon float was placed in the cylinder on top of the solution. Any headspace or trapped air was released by tilting the cylinder and pressing down on the float which forced the air along a groove in the float out of the cylinder. The cylinder was then placed on an asbestos pad on top of a magnetic stir pad. This prevented heat transfer from the mixer to the cylinder of solution. This entire setup was placed in a covered vessel and allowed to stir for a minimum of 18 hours. The use of the covered vessel prevented incidental UV light from promoting the degradation of the VOCs in solution. The 18 hour minimum time for mixing was based on guidance from Mr Thomas Speth at the EPA in Cincinnati, Ohio. Although the VOCs used are relatively insoluble in water, they solubilize to some extent with time and agitation as long as the solution does not reach saturation. In these experiments, most stir times exceeded 24 hours and no problems were experienced in getting the VOCs into solution.

This same procedure was used for preparing the single

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component VOC solutions. Amounts injected into each mix, whether single or a combination of all four, are listed in Tables 3.4 and 3.5.

The final end products of the VOC destruction are water, carbon dioxide and chlorine and hydrogen ions. The following four stoichiometric equations illustrate this and also show the molar ratios of H_2O_2 to the VOC of interest.

1.2 DCE

$$C_2H_2Cl_2 + 3H_2O_2 \longrightarrow 2H_2O + 2CO_2 + 2Cl^- + 4H^+$$

TCE

$$2C_2HCl_3 + 5H_2O_2 \longrightarrow 2H_2O + 4CO_2 + 6Cl^- + 8H^+$$

Dichloromethane

$$CH_2Cl_2 + 2H_2O_2 \longrightarrow 7H_2O + CO_2 + 2Cl^- + 2H^+$$

Benzene

$$C_6H_6 + 7H_2O_2 \longrightarrow 2H_2O + 6CO_2 + 16H^+$$
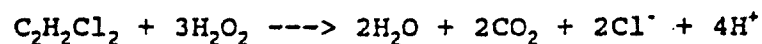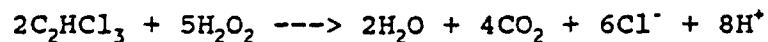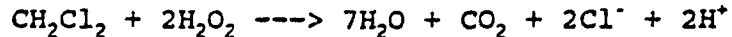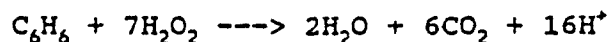
To obtain the desired concentration(s) of VOC in the synthetic wastewater which was fairly consistent with the average concentrations of the VOCs at Anniston Army Depot, the following equation was solved.

{[desired conc. x cyl. vol.] / 1000mg/L} / VOC density
= amount of VOC added

1,2 DCE

$$\{[7.368 \text{ mg/L} \times 1.67 \text{ L}] / 1000 \text{ mg/L}\} / 1.4435 \text{ g/ml}$$

$$= .008524 \text{ ml or } 8.524 \text{ ul}$$

TCE

$$\{[2.970 \text{mg/l} \times 1.67 \text{ L}] / 1000 \text{ mg/L}\} / 1.456 \text{ g/ml}$$

$$= .003406 \text{ ml or } 3.406 \text{ ul}$$

Dichloromethane

$$\{[.480 \text{ mg/L} \times 1.67 \text{ L}] / 1000 \text{ mg/L}\} / 1.316 \text{ g/ml}$$

$$= .0006013 \text{ ml or } .6018 \text{ ul}$$

Benzene

$$\{[.110 \text{ mg/L} \times 1.67 \text{ L}] / 1000 \text{ mg/L}\} / .8787 \text{ g/ml}$$

$$= .0002065 \text{ ml or } .2065 \text{ ul}$$

Table 3.4 VOCs injected in Flow-through Experiments

	Exp 1 (ul)	Exp 2 (ul)	Exp 3 (ul)
1,2 DCE	14.0	13.8	14.0
TCE	4.0	4.0	3.0
Dichloromethane	1.2	1.0	1.0
Benzene	0.9	1.0	0.8

Table 3.6   VOCs injected in Batch Experiments

Batch	1,2 DCE (ul)	TCE (ul)	Dichloro-methane (ul)	Benzene (ul)
1,2 DCE	14.0			
TCE		4.0		
Dichloromethane			2.9	
Benzene				9.0
Combination of Four VOCs	14.0	3.0	1.0	1.0

When the cylinder containing the synthetic wastewater was removed from the covered vessel, it was placed on the same asbestos pad above a magnetic stirrer in preparation for connection to the thin film reactor setup. First, several samples were taken from the cylinder by opening the teflon valve on the cylinder's exit port and allowing the synthetic wastewater to fill the 15 ml vials. After the initial samples were taken the teflon float was removed and a predetermined amount of hydrogen peroxide injected. Table 3.6 lists the amounts injected.

The determination of the volume of H_2O_2 required to react with the synthetic wastewater containing the four VOCs at the Anniston Army Depot concentration levels follows. From the preceding calculations it can be seen that the VOC to H_2O_2 molar ratio for destruction of the VOC is as follows:

```
1,2 DCE              1 : 3
TCE                  2 : 5
Dichloromethane  1 : 2
Benzene              1 : 7
```

Using these ratios, the stoichiometric volume was calculated as follows:

	g/mole	conc. mg/L	moles per liter mg/L x mg/mole (in mM/liter)	Factor in mMoles
1,2 DCE	96 g/mole	7.368	.07675 x 3	.2303
TCE	130 g/mole	2.970	.02285 x 2.5	.05713
Dichlorometh.	84 g/mole	.480	.00571 x 2	.01142
Benzene	78 g/mole	.110	.00141 x 7	.00987

* mMoles of H_2O_2 per liter of synthetic wastewater   .3087

.3087 mMole H_2O_2/L x 34g H_2O_2/mMole H_2O_2 = .0105 g/L

.0105g H_2O_2/L x 1ml H_2O_2/ 1.4422g H_2O_2 x 1/0.30

= .02427 ml H_2O_2/ L synthetic wastewater

or 24.27 ul H_2O_2 per liter synthetic wastewater

Since D. Pinto (1991) found 2 to 3 times stoichiometric ratio was the optimum range for good destruction rates, 100 ul of H_2O_2 was added to each 1670 ml of synthetic wastewater. The actual amounts injected are listed in Table 3.6.

Table 3.6   Hydrogen Peroxide Injections in ul.
```
    Batch, 1,2 DCE Pure ....................  99
    Batch, TCE Pure .......................  98
    Batch, Dichloromethane ................ 100
    Batch, Benzene ........................ 100
    Batch, Mixture of 4 VOCs .............. 100
    Flow-through, Exp 1 ................... 100
    Flow-through, Exp 2 ...................  90
    Flow-through, Exp 3 ................... 100
```

The hydrogen peroxide (H_2O_2) added in each instance was well in excess of the molar ratio required for VOC destruction. Varying the molar concentration of H_2O_2 to VOC was not evaluated but rather was held at a consistent volume throughout the experimentation.

After stirring the synthetic wastewater mixture for ten minutes, several samples were again taken for analysis of the synthetic wastewater after the addition of the H_2O_2. These samples represent the 100% values on all of the graphs and figures. It is at this concentration of VOC(s) present in the synthetic wastewater that the measurement of destruction began. After sampling was completed the cylinder was connected to the flow-through setup for start of either the batch or flow-through experimentation.

3.2 Analytical Methods

All samples were analyzed under the provisions of EPA Method 8240. Each sample was purged using a Tekmar Purge and Trap Concentrator and then analyzed in a Hewlett Packard (HP) 5890 A Gas Chromatograph with an HP 5970 Mass Selective Detector (MSD). The HP 59940 A ChemStation is the controller for this GC/MS system and it is here that the instrument data results are integrated and analyzed and then placed in a final report.

Summary of Method

The VOCs were introduced into the gas chromatograph by a Tekmar, Model LSC-2, purge and trap device. The components present were separated via the gas chromatograph and detected using the mass spectrometer, which provided both qualitative and quantitative information.

The sample was prepared by filling a 5 ml gas-tight syringe with the solution from one of the 15 ml sample vials. Then 10 ul of surrogate solution (system monitoring compounds) and 10 ul of the mid level volatile internal standards were injected into the 5 ml syringe. The contents of the 5 ml syringe were then injected into the purging chamber. Table 3.7 presents information on the surrogate and volatile internal standards solution. Each solution was prepared under the guidelines of EPA Method 8240. For quantitation purposes,

Table 3.7 Characteristic Ions for the Surrogate and Internal
Standards for Volatile Organic Compounds.

Compound	Primary Ion	Secondary Ion(s)
Surrogate		
4-Bromofluorobenzene	95	174, 176
1,2 Dichloroethane-d_4	65	102
Toluene-d_8	98	70, 100
Internal Standards		
Bromochloromethane	128	49, 130, 51
1,4-Difluorobenzene	114	63, 88
Chlorobenzene-d_5	117	82, 119

1,2 DCE and Dichloromethane were quantitated using

Bromochloromethane while TCE and Benzene were quantitated with

1,4-Difluorobenzene.

Helium, the purge gas, was bubbled through the solution

at ambient temperature, and the volatile components were

transferred from the aqueous phase to the vapor phase. The

vapor was then swept through a sorbent column (trap) where the

VOCs were trapped. Upon purge completion, the sorbent column

was heated and backflushed with helium to desorb the

components onto a gas chromatograph column. The GC column was

then heated to elute the components which were detected with

the mass spectrometer. Table 3.8 presents the GC column data.

Retention times for the first column are listed in Table 3.9.

Table 3.8   Gas Chromatograph Column Specifications

    Column 1   supplier SUPELCO
                  1% SP™-1000 Support
                  60/80 Mesh CARBOPACK™ B Column
                  6 foot x ¼ in. stainless steel

    Column 2   suppler SUPELCO
                  1% SP™-1000 Support
                  60/80 Mesh CARBOPACK™ B Column
                  2.0 meter x ¼ in. O.D. Glass

----

note: All experiments except Flow-through Exp. 1 were analyzed
      with Column 1.

    The following are the purge and trap analytical
conditions:

Purge Conditions

            Purge Gas: Helium
            Purge Time: 11.0 ± 0.1 min.
            Purge Flow Rate: 25-40 ml/min.
            Purge Temperature: Ambient

Desorb Conditions

            Desorb Temperature: 180°C
            Desorb Flow Rate: 15 ml/min.
            Desorb Time: 4.0 ± 0.1 min.

Trap Bake Conditions

            Bake Temperature: 220°C
            Bake Time: 8.0 ± 0.1 min.

Trap Reconditioning Conditions

            Reconditioning Temp: 180°C
            Reconditioning Time: 30 min.

    The following are the Gas Chromatograph analytical
conditions:

            Carrier Gas: Helium
            Flow Rate: 30 ml/min.
            Initial Temperature: 45°C
            Initial Hold Time: 3.0 min.

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```
Ramp Rate:              8°C/min.
Final Temperature:      220°C
Final Hold Time:        Until all target
                        compounds elute.
```

The GC/MS was tuned daily, or every 12 hours of use by using the AUTOTUNE method available in the ChemStation controller. Prior to sample analysis, a method blank was analyzed. Additionally, the purge and trap device was conditioned daily or every 12 hours of use. The standard curve for Column 1 was performed on 23 Oct 1991.

Table 3.9 VCC Retention Times for Column 1

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Chloromethane	1.393	50.0	52, 49
Bromomethane	2.150	94.0	96, 79
Vinyl Chloride	2.753	62.0	64, 61
Chloroethane	3.771	61.0	66, 49
Dichloromethane	5.725	84.0	49, 51, 86
Acetone	6.528	43.0	58
1,1-Dichloroethene	8.401	96.0	61, 98
Bromochloromethane(I)	8.964	128.0	49, 51, 130
1,1-Dichloroethane	9.710	63.0	65, 83
trans 1,2-DCE	10.469	96.0	61, 98
Chloroform	11.093	83.0	85, 47
1,2-Dichloroetane-d$_4$	11.703	65.0	102
2-Butanone	11.759	43.0	43, 72
1,2-Dichloroethane	11.823	62.0	64, 98
1,1,1-Trichloroethane	13.143	97.0	99, 117
Carbon Tetrachloride	13.502	117.0	119, 121
Bromodichloromethane	14.146	83.0	85,129
1,2-Dichloropropane	15.441	63.0	62, 41
cis-1,3-Dichloropropene	15.726	75.0	77, 39
Trichloroethene	16.296	130.0	95, 97, 132
Benzene	16.730	78.0	52, 71
Chlorodibromomethane	17.008	129.0	208, 206
trans-1,3-Dichloro-propene	17.056	75.0	77, 39
1,1,2-Trichloroethane	17.088	97.0	83, 85, 99
1,4-Difluorobenzene(I)	19.329	114.0	63, 88
Bromoform	19.844	173.0	171, 175, 252
2-Hexanone	20.157	43.0	58, 57, 100
4-Methyl.2-Pentanone	21.784	43.0	58, 57, 100
Tetrachloroethene	22.118	164.0	129, 131, 166
1,1,2,2-Tetra-chloroethane	22.192	83.0	85, 131, 133
Toluene-d$_8$	23.164	98.0	70, 100
Chlorobenzene-d$_5$	24.517	117.0	82, 119
Chlorobenzene	24.612	112.0	114, 177
Ethylbenzene	26.575	106.0	91
4-Bromofluorobenzene	29.207	95.0	174, 176
Styrene	30.598	104.0	104, 103, 78, 51, 77
Xylene	31.976	106.0	91

4 Results and Discussion

4.1 Results

Batch Tests

In each batch test performed, the destruction of the four VOCs was observed as either a single component or as part of the mixture of all four. Table 4.1 lists the starting and ending concentrations for each VOC. Appendix A lists the concentration and per cent remaining at each sampling.

Figures 4.1 through 4.4 depict the destruction of the VOCs over the course of 25 minutes. The figures show that good destruction was obtained for single components in 10 minutes or less - 99% for all but dichloromethane, where only 50% destruction was found at 10 minutes. After 25 minutes 1,2 DCE was reduced by 81.3%.

The mixed compounds required approximately 20 min. for 99% destruction, except dichloromethane where only 80% destruction was obtained at 25 minutes.

Table 4.1 VOC Concentrations in each Batch Test

Batch		Concentration (ppb) start	end	% destruction
1,2 DCE	alone	6335.0	5.4	99.91
	in mix	4431.0	1.4	99.97
TCE	alone	2577.0	29.0	98.87
	in mix	2035.0	11.0	99.46
Dichloro-	alone	1685.0	350.0	79.23
methane	in mix	714.1	138.0	80.67
Benzene	alone	78.36	6.98	91.09
	in mix	919.4	7.3	99.21

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Fig. 4.1 1,2 DCE Concentration
## Batch Test Experiments
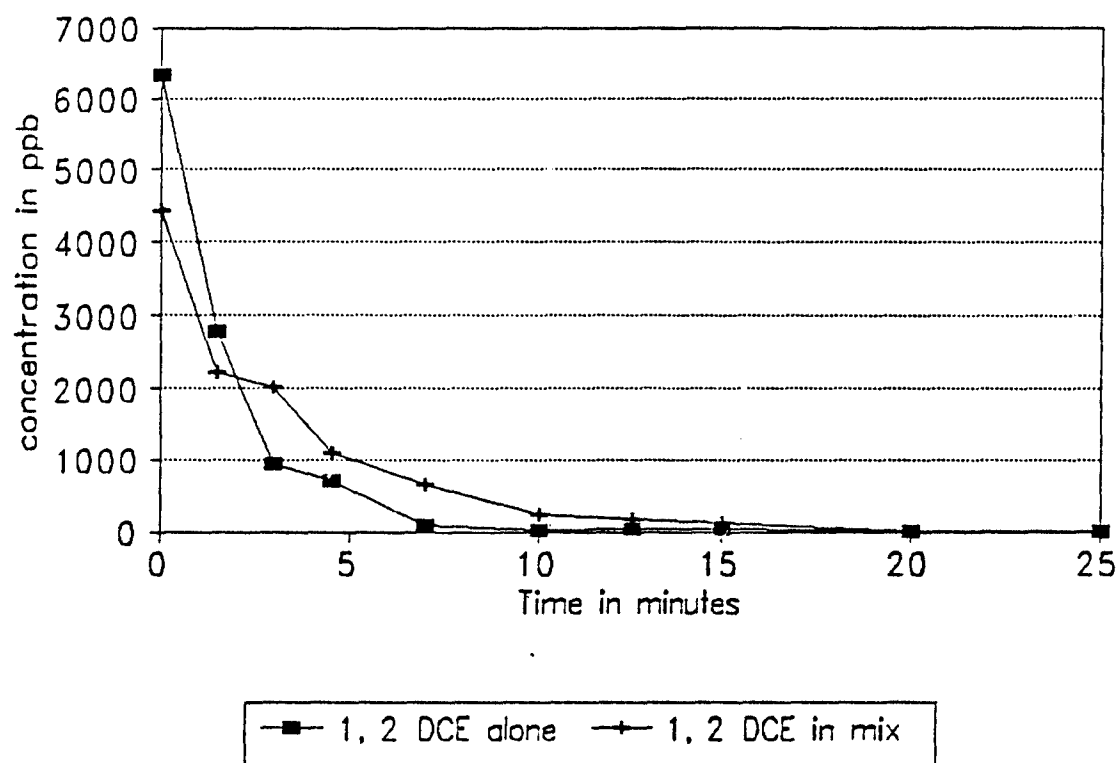
Fig. 4.2 TCE Concentration
Batch Test Experiments
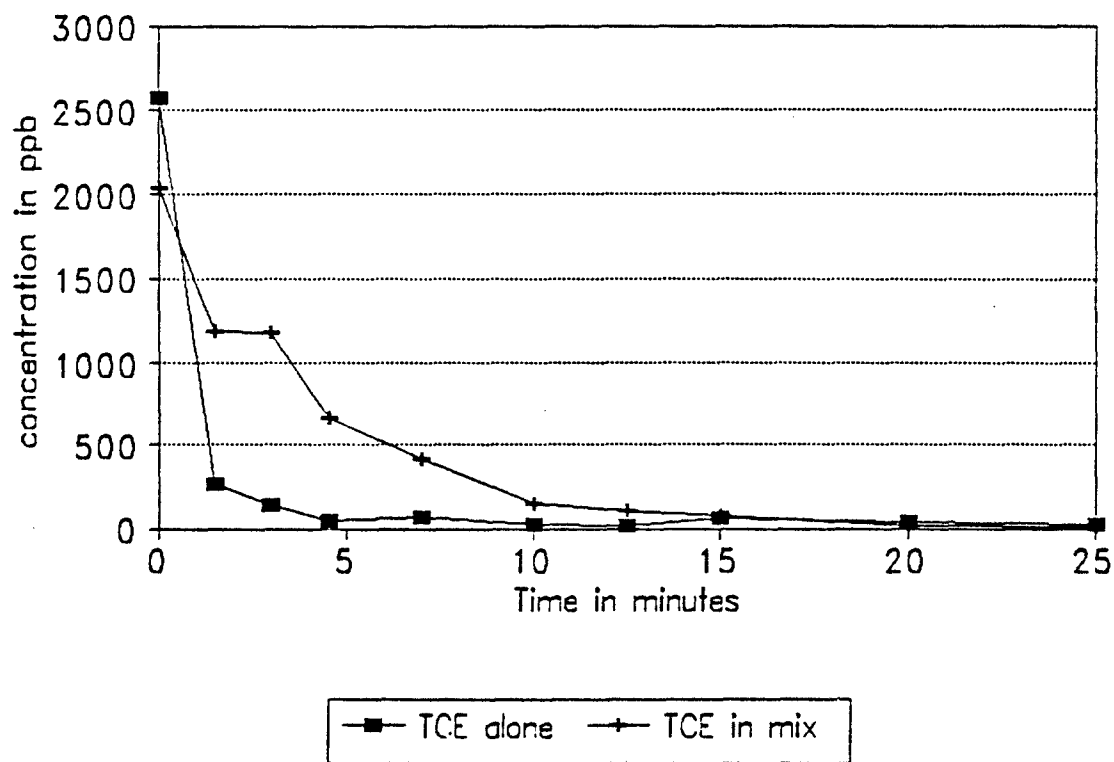
# Fig. 4.3 Dichloromethane Concentration
## Batch Test Experiments

Fig. 4.4 Benzene Concentration
Batch Test Experiments

Legend: Benzene alone — Benzene in mix
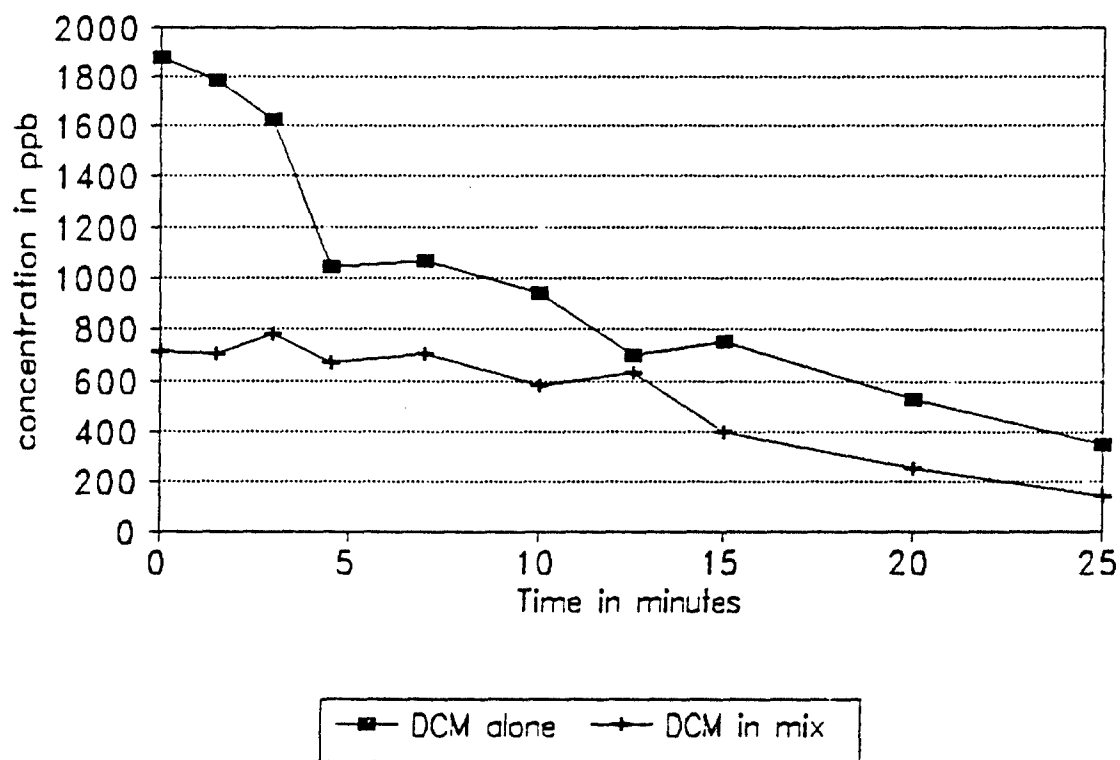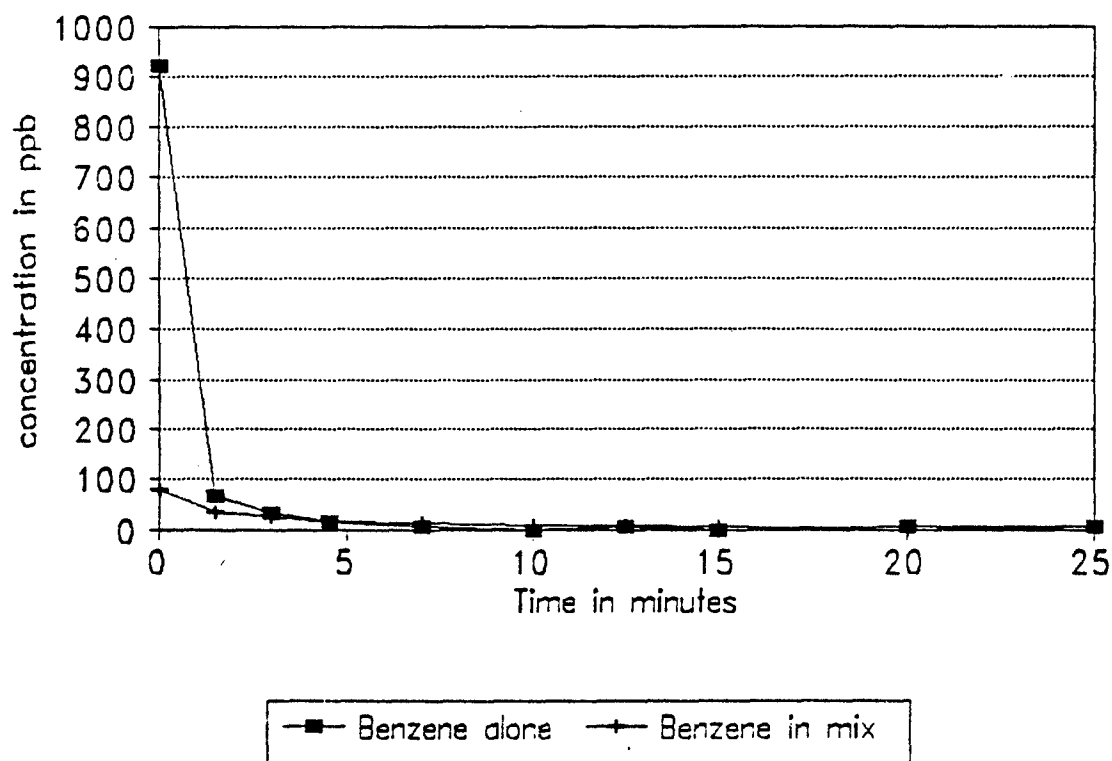
Flow-through Experiments

As with the batch tests there was significant destruction of all of the VOCs except for dichloromethane. Table 4.2 lists the starting and ending concentrations for this set of experiments. Appendix A contains the concentrations and per cent remaining data for each of the VOCs in each experiment.

Figures 4.5 through 4.8 depict the destruction (or buildup) of the VOCs over the course of the three experiments. The times shown are contact time when the solution is in the reactor and contacting UV light. Although the starting concentrations and times for each flow-through experiment were slightly different, the three experiments show good reproduce-ability.

Table 4.2   VOC Concentration in each Flow-through
Experiment

| | Concentration in ppb | | | | | |
| | ** Exp 1 ** | | ** Exp 2 ** | | ** Exp 3 ** | |
	start	end	start	end	start	end
1,2 DCE	6401.0	75.5	6589.0	329.4	4649.0	nd
TCE	3682.0	135.5	3463.0	369.4	1820.0	nd
Dichloro-methane	750.8	934.5	1095.0	1107.0	709.4	408.9
Benzene	45.3	nd	106.8	nd	114.2	nd

Fig. 4.5 1,2 DCE Concentration
## Flow-through Experiments
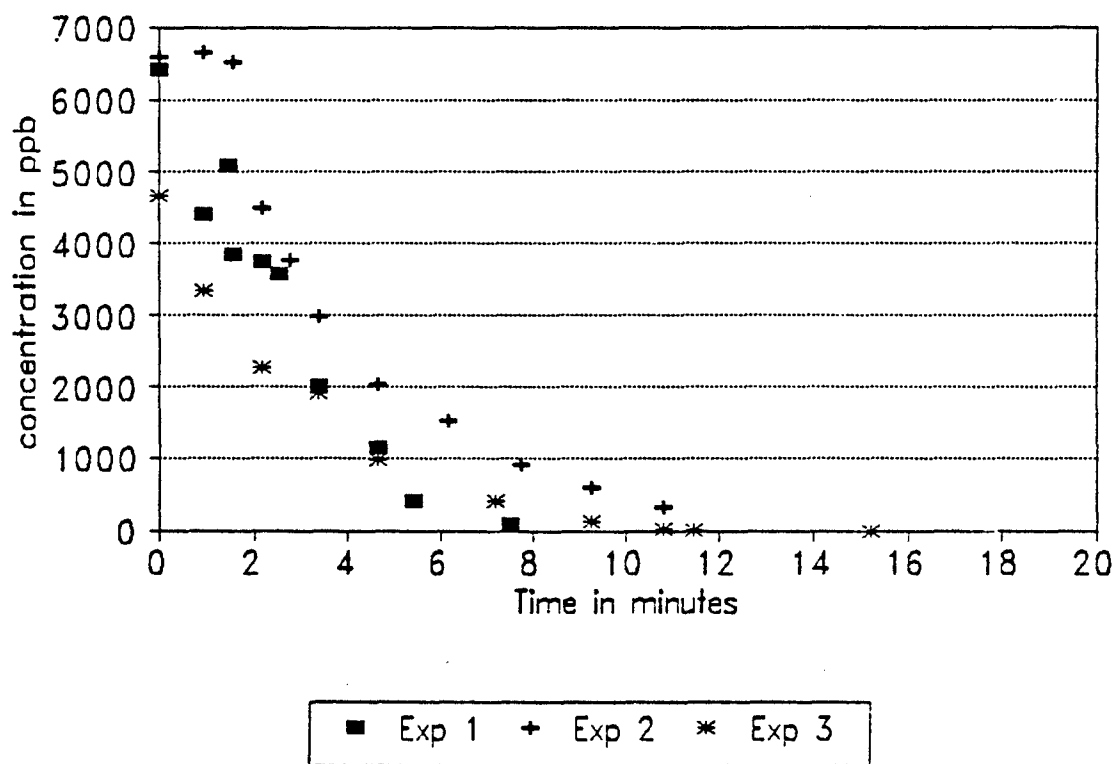
Fig. 4.6 TCE Concentration
Flow-through Experiments
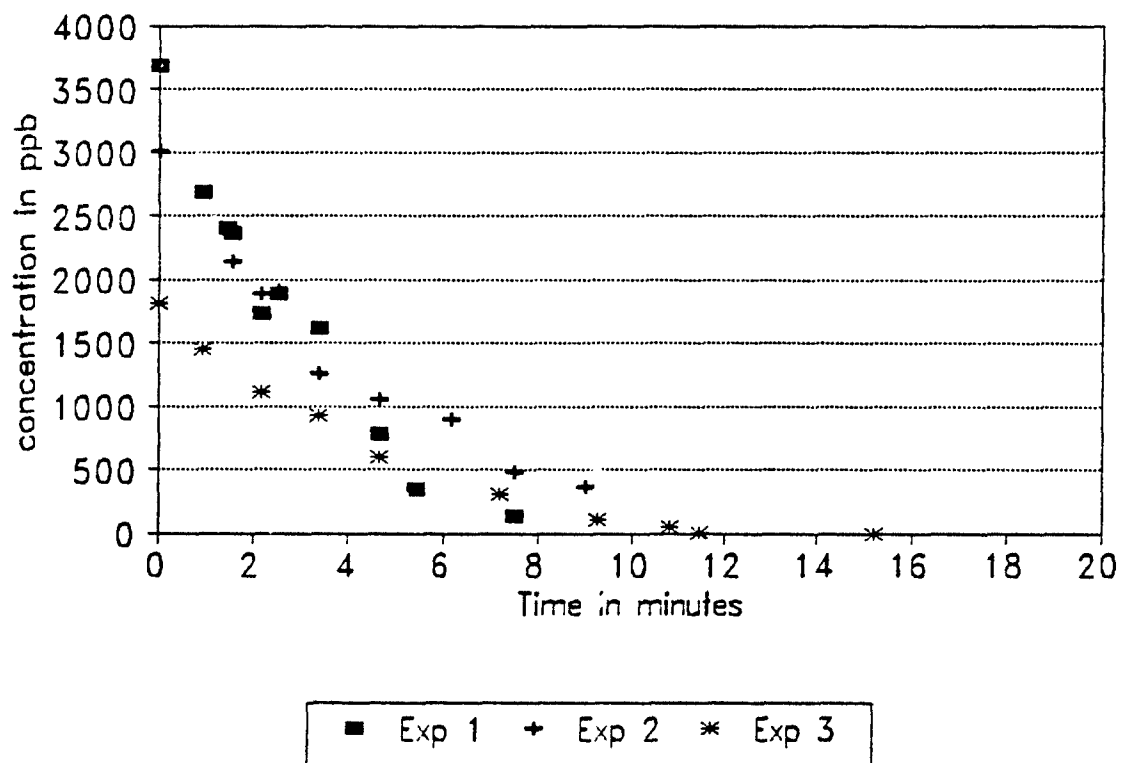
Fig. 4.7 Dichloromethane Concentration
## Flow-through Experiments
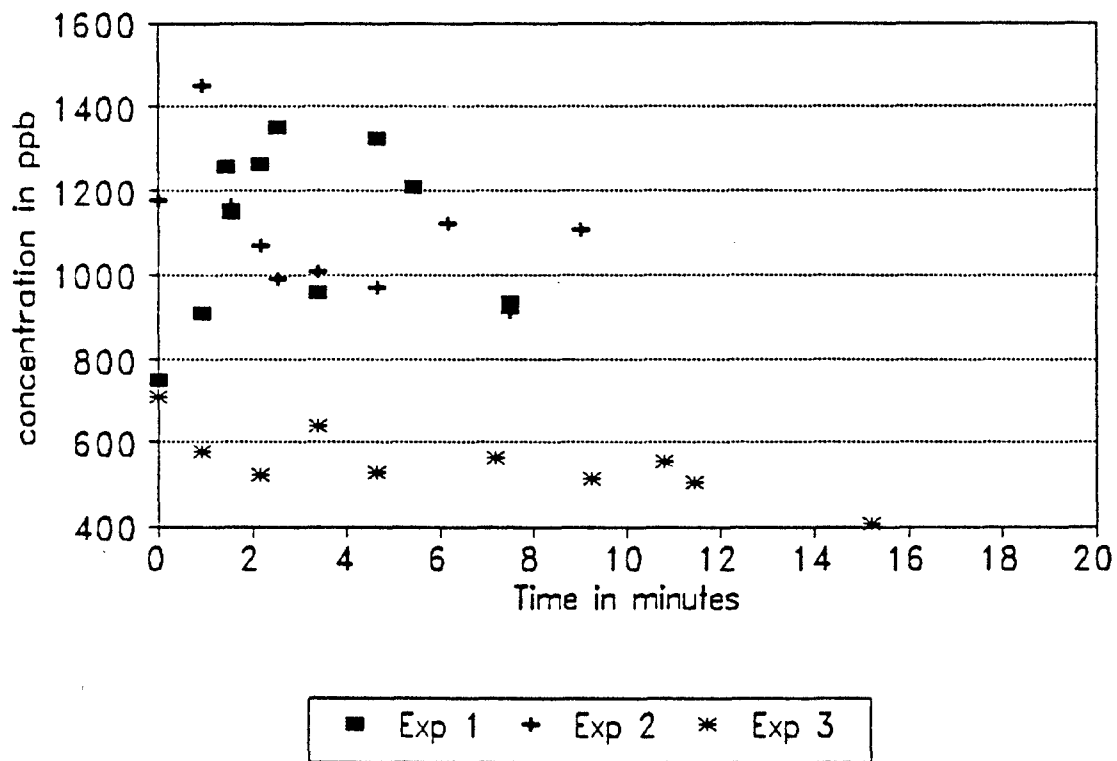
Fig. 4.8 Benzene Concentration
Flow-through Experiments
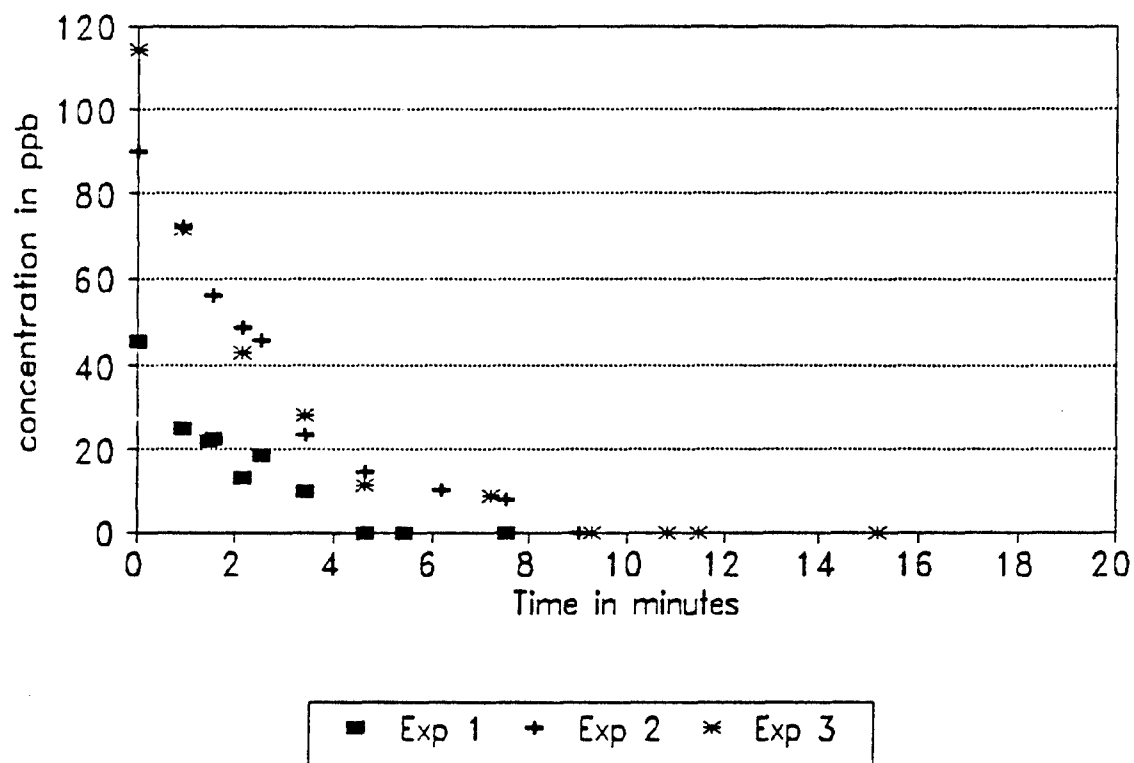
4.2 Discussion

Batch Tests

Figures 4.1 through 4.4 portray the destruction of the target compounds as either the sole component or as part of the four VOC mix. In each case other than dichloromethane, the destruction proceeds to detectable limits of each compound. Even though dichloromethane concentration levels did not decline to detectable limits, it was significantly reduced. The majority of destruction occured within ten minutes for each VOC other than dichloromethane.

Plotting the per cent of VOC remaining versus time on a semi-log plot presents a nearly linear trend. Figures 4.9 through 4.12 depict this. An exponential line was fit to the semi-log plot of the fraction of VOC remaining. To develop these lines, all concentration levels down to and including the first point below detectable quantitation limits were used. The GRAPHER software package was used to integrate these lines as seen on the graphs. Table 4.3 lists all of these "best fit" equations for both the batch and flow-through experiments.

The destruction of VOCs in the batch tests as either a single component or as part of the four VOC mixture were similar, with only slightly differing rates of destruction. The overall rates of destruction were faster for the VOCs as a sole component than when a component of the mix. The dichloromethane rates appear to be identical. However the

Fig 4.9   1, 2 DCE Destruction
Batch Test Experiments

1, 2 DCE alone start 6335 ppb
end 11.75 ppb

1,2 DCE Mix start 4431 ppb
end   1.4 ppb

□ DCE alone   *   DCE in mix
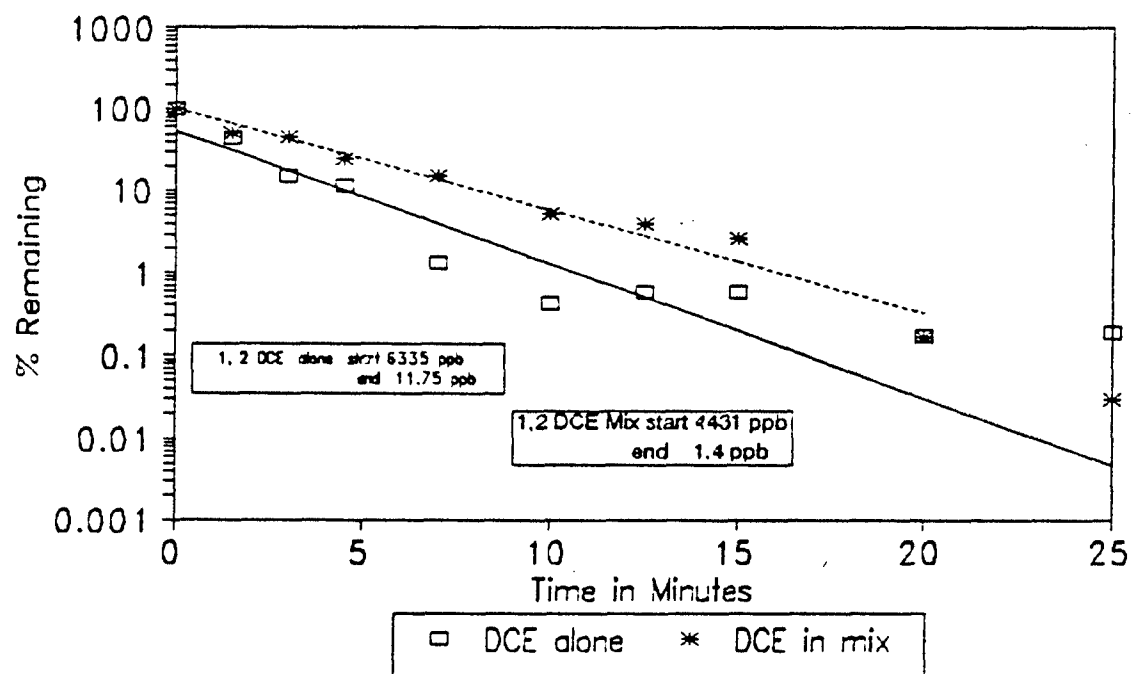
Fig 4.10 TCE Destruction
Batch Test Experiments

TCE Pure start 2577 ppb
and   29 ppb

TCE mix start 2035 ppb
and 11.2 ppb

% Remaining

Time in Minutes

□ TCE alone   ∗ TCE in mix
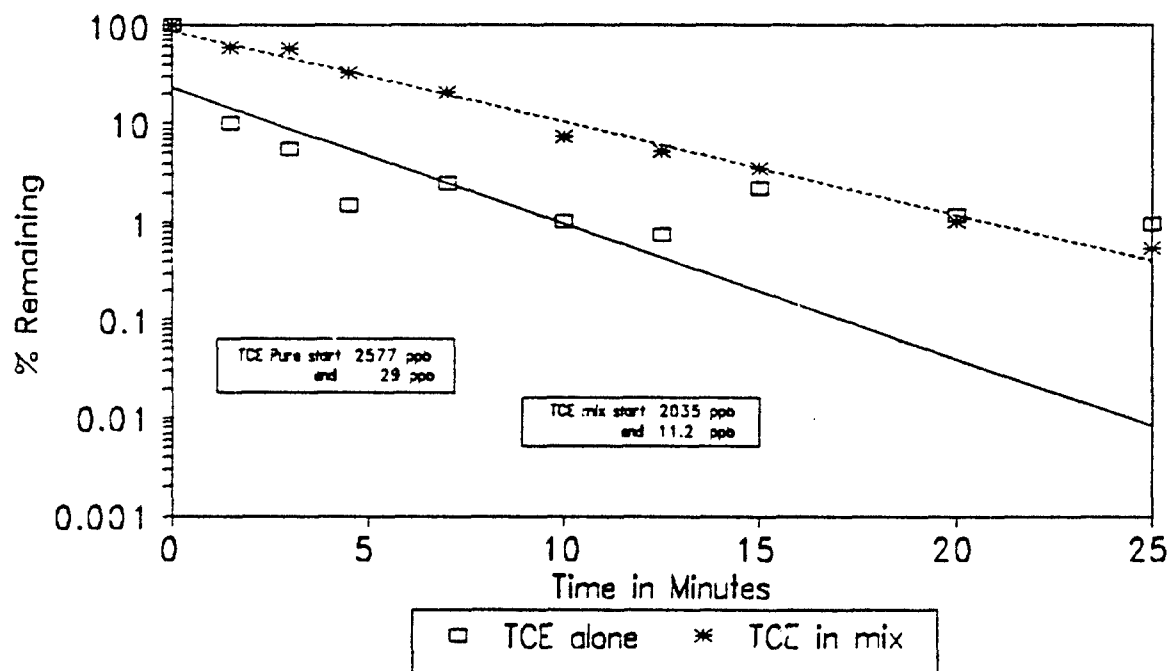
Fig 4.11 Dichloromethane Destruction
Batch Test Experiments

Dichloromethane alone start 1877 ppo
and 350 ppo

Dichloromethane mix start 714.1 ppo
and 138 ppo

□ DCM alone   ✳ DCM in mix

y-axis: % Remaining
x-axis: Time in Minutes
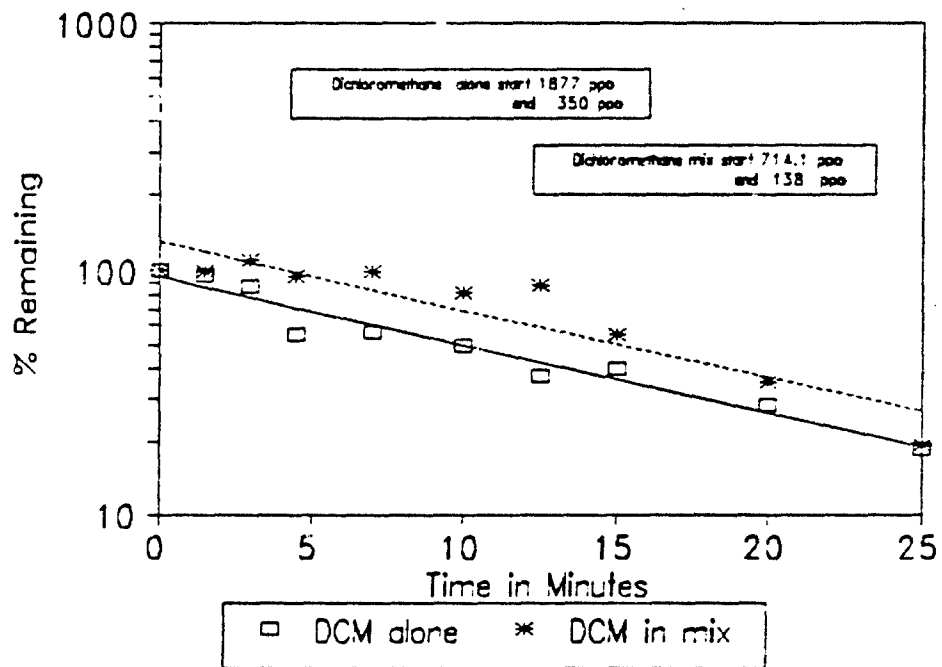
Fig 4.12   Benzene Destruction
Batch Test Experiments

Benzene alone start 78.36 ppb
end 6.38 ppb

Benzene Mix start 919.4 ppb
end   7.3 ppb

% Remaining

Time in Minutes

□   Benzene alone   ✳   Benzene in mix
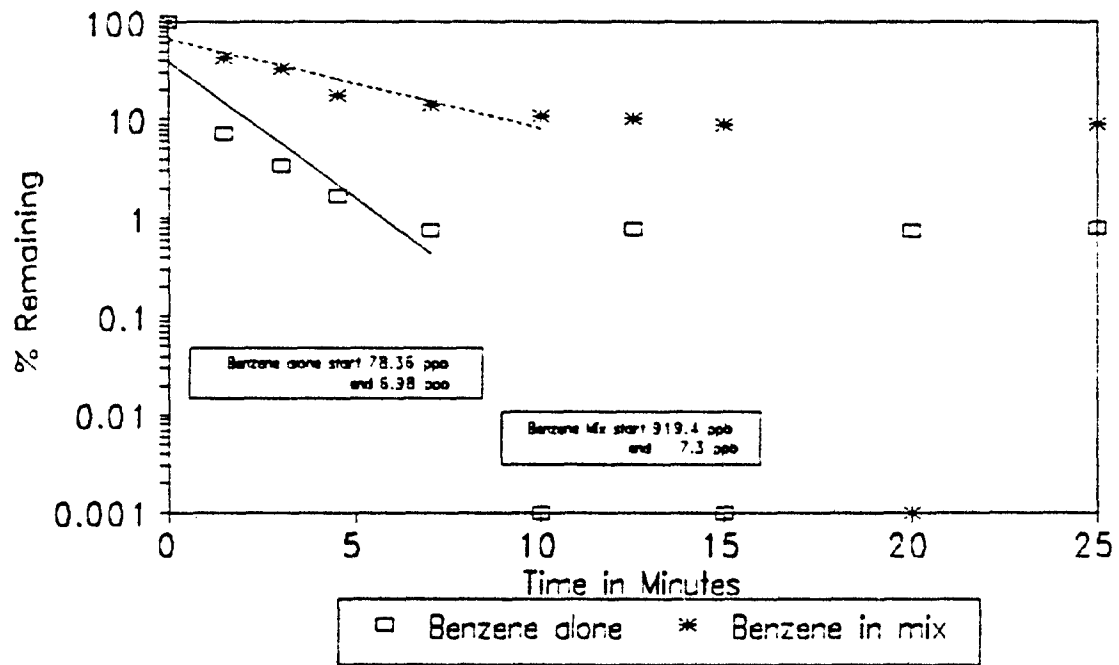
Table 4.3 GRAPHER Best Fit Equations

Batch Test Experiments

1,2 DCE alone $y = EXP(-0.373337x) * 53.6765$
TCE alone $y = EXP(-0.317433x) * 22.9576$
DCM alone $y = EXP(-0.0641622x) * 94.513$
Benzene alone $y = EXP(-0.640389x) * 38.5171$

1,2 DCE in mix $y = EXP(-0.286862x) * 101.794$
TCE in mix $y = EXP(-0.214464x) * 87.2078$
DCM in mix $y = EXP(-0.0631443x) * 130.072$
Benzene in mix $y = EXP(-0.211432x) * 66.4078$

Flow-through Experiments

Exp 1 1,2 DCE $y = EXP(-0.435959x) * 168.514$
        TCE $y = EXP(-0.367443x) * 129.773$
        DCM $y = EXP(+0.0140522x) * 138.155$
        Benzene $y = EXP(-0.399947x) * 101.658$

Exp 2 1,2 DCE $y = EXP(-0.288209x) * 125.683$
        TCE $y = EXP(-0.203898x) * 102.43$
        DCM $y = EXP(-0.0158411x) * 106.821$
        Benzene $y = EXP(-0.321554x) * 108.687$

Exp 3 1,2 DCE $y = EXP(-0.550441x) * 225.861$
        TCE $y = EXP(-0.351326x) * 150.455$
        DCM $y = EXP(-0.0187309x) * 88.8347$
        Benzene $y = EXP(-0.360551x) * 91.4648$

DCM stands for dichloromethane

----

equations in Table 4.3 show that as a single component, dichloromethane had a greater rate of destruction than when in a mixture.

Since each batch test was dosed with 100ul of H_2O_2, 2.47 times the stoichiometric molar ratio required for destruction by UV/H_2O_2 oxidation, sufficient hydroxyl radicals should have been present to promote oxidation in each test. Competing reactions within the four VOC mixture resulted in slower rates of destruction when compared with those rates for single component destruction. Not only is competition for the hydroxyl radicals and UV photons occurring, but a strong interaction was likely taking place between the four VOCs themselves as the oxidation process occured.

The semi-log plots of the fraction of VOC remaining versus time tend to be linear. This suggests, as found by other researchers, that the reactions are pseudo first order.

Flow-through Tests

As with the batch tests, the flow-through experiments exhibited remarkably similar destruction rates. Once again the dichloromethane showed a much slower rate of destruction than the other VOCs. Actually, in Experiment One, it appeared to have been produced. Later experiments showed this not to be the case.

The semi-log plots of fraction of VOC remaining versus time indicate a pseudo first order reaction rate, as shown in Figures 4.13 through 4.16. In developing best fit lines by GRAPHER, all the data were used for Experiments One and Two. Incomplete destruction was observed over the short contact times of Experiments One and Two.

Based on these observations, the time for Experiment Three was extended. As in the batch test the calculation for the best fit line for Experiment Three included only those data to the first point below detectable limits. With a longer reaction time concentrations were reduced to the limits of detection for 1,2 DCE, TCE and benzene, but not for dichloromethane.

The apparent increase in concentration of dichloromethane in Experiment One pointed to the hypothesis that it was being produced by the destruction of one of the other compounds present. This in turn led to the batch test of each compound alone to determine if intermediates were being produced in significant concentration, especially dichloromethane. No

Fig 4.13 1,2 DCE Destruction
Flow-through Experiments

Exp 1 start 6401 ppb
         end 75.5 ppb

Exp 2 start 6589 ppb
         end 329.4 ppb

Exp 3 start   4649 ppb
       9.82 min 114.6 ppb
         end   n.d.

Legend:
- ■ Exp 1 + Exp 2 ✳ Exp 3
- .... Exp 1 ------ Exp 2 —— Exp 3

Y-axis: % Remaining
X-axis: Time in Minutes
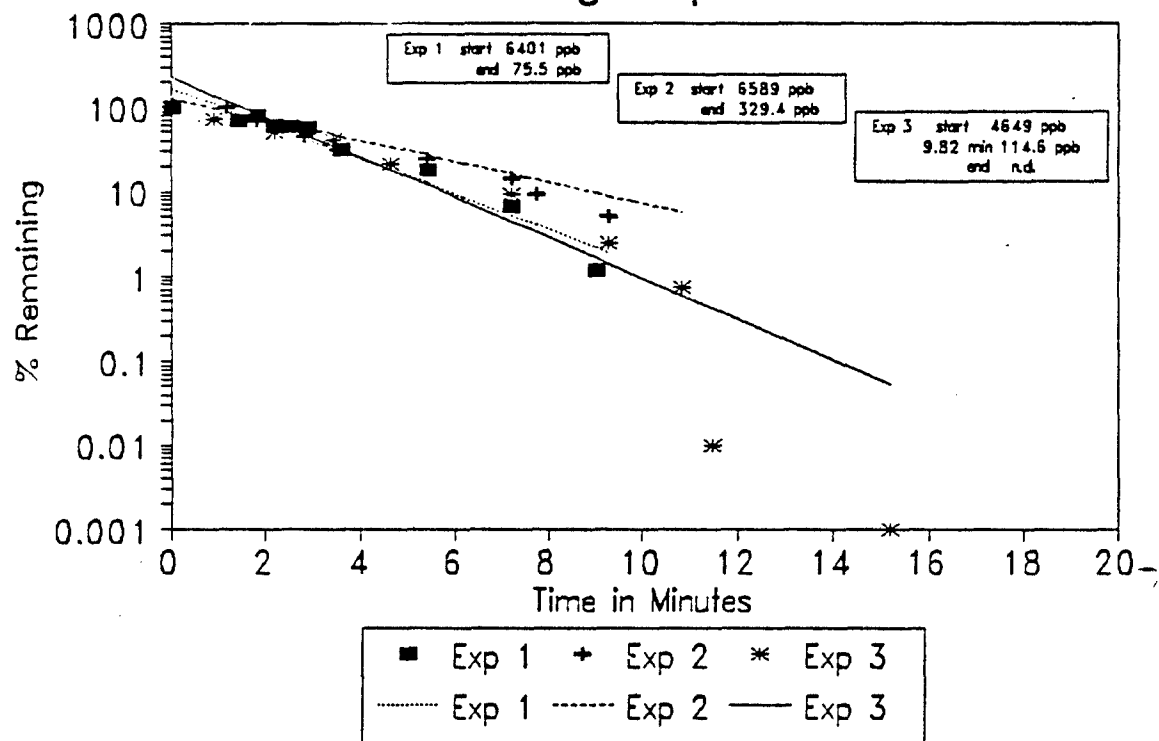
Fig 4.14 TCE Destruction
Flow-through Experiments

Exp 1 start 3682 ppb
      end 135.5 ppb

Exp2 start 3141 ppo
      end 369.4 ppb

Exp 3 start 1820 ppo
      9.82 min 107.9 ppb
      end 8.02 ppo

% Remaining (y-axis)

Time in Minutes (x-axis)

■ Exp 1   + Exp 2   ＊ Exp 3
········· Exp 1   ------ Exp 2   ——— Exp 3
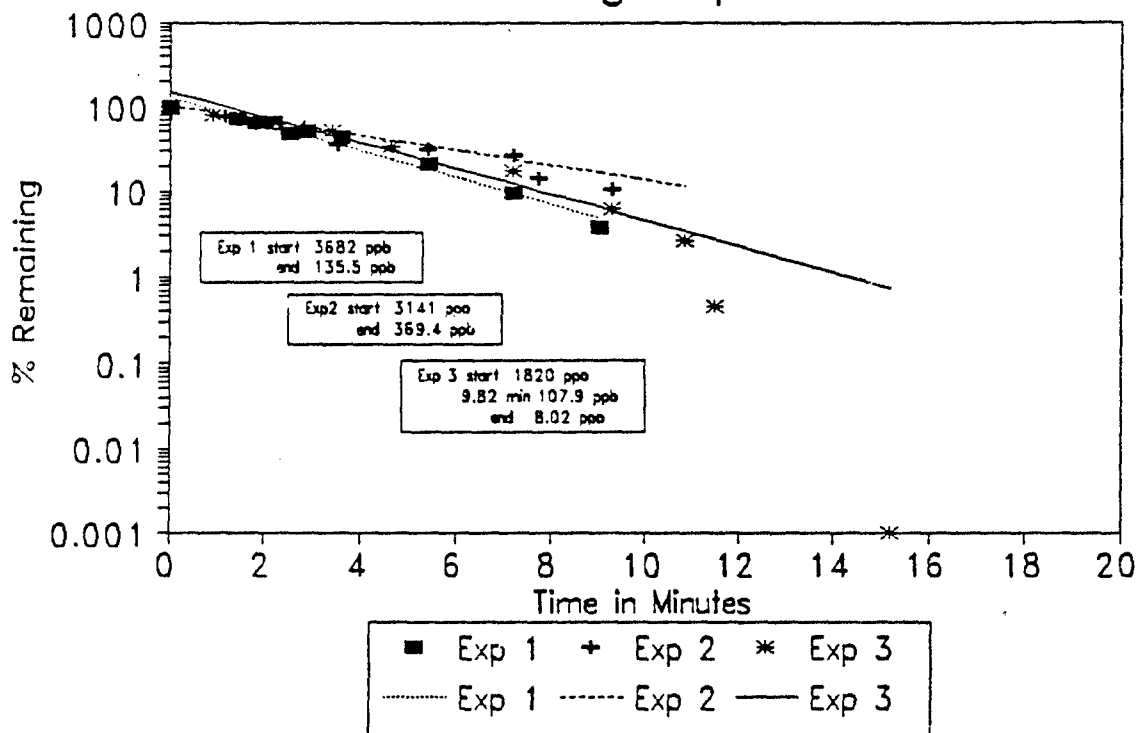
Fig 4.15 Dichloromethane Destruction
Flow-through Experiments

Exp 1 start 750.8 ppb
end 934.5 ppb

Exp 2 start 1083.5 ppb
end   1107.0 ppb

Exp 3 start 709.4 ppb
9.82 min 513.8 ppb
end   408.9 ppb

Time in Minutes

■ Exp 1   + Exp 2   ✳ Exp 3

------- Exp 2 ——— Exp 3

Fig 4.16 Benzene Destruction
Flow-through Experiments

Fig 4.16 Benzene Destruction — Flow-through Experiments. Plot of % Remaining (log scale, 0.001 to 1000) versus Time in Minutes (0 to 20).

Exp 1 start 45.3 ppb
end n.d.

Exp 2 start 106.7 ppb
end n.d.

Exp 3 start 98.8 opb
9.82 min n.d.
end n.d.

Legend:
■ Exp 1   + Exp 2   * Exp 3
········· Exp 1   ------- Exp 2   —— Exp 3
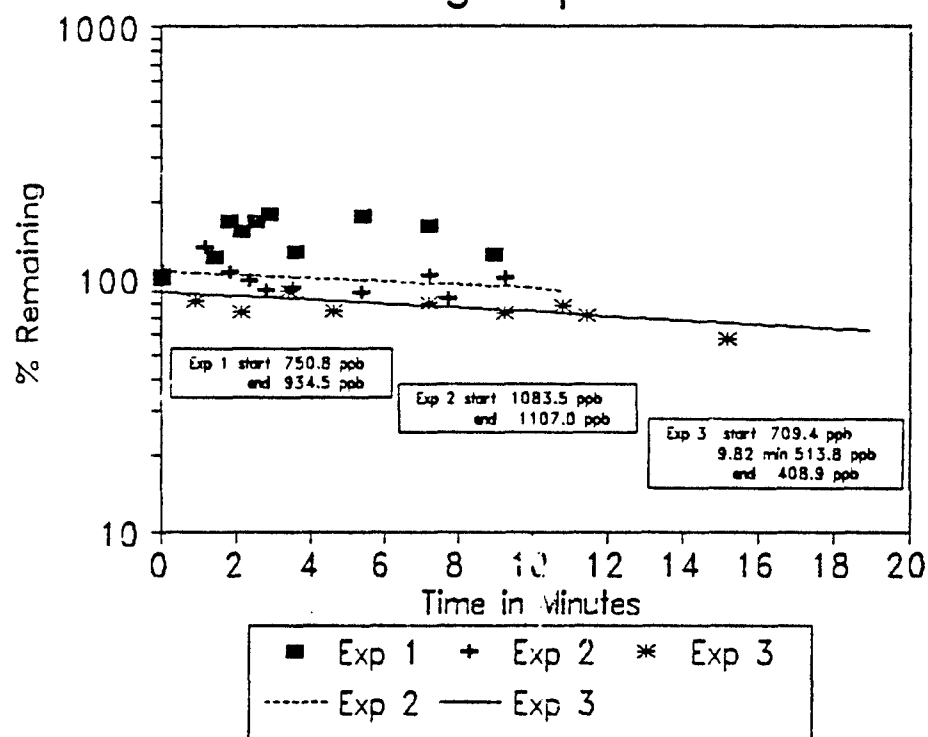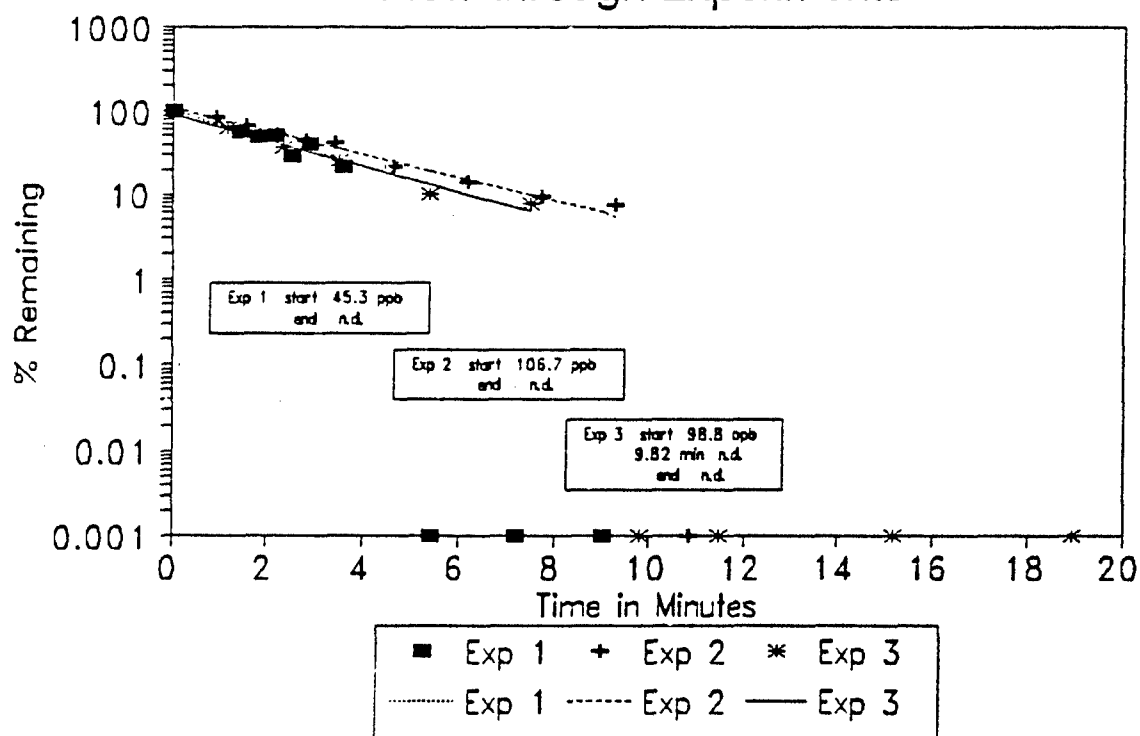
significant concentrations of intermediates were found to be present during these batch tests. Any compounds present other than the VOCs of interest, surrogate or volatile internal standard were also found in the method blank. They were commonly found to be chloroform, acetone and 2-butanone. The method blank is nothing more than Super Q water plus 10ul each of surrogate and internal standard.

It was concluded that the increase in dichloromethane corresponded to the significant use of dichloromethane for extractions and other lab procedures being performed at the same time Experiment One samples were being analyzed on the GC/MS. Dichloromethane has been found to be a problem contaminant with GC/MS analysis in other instances. The batch tests discount the production of dichloromethane and Experiment Three, the last flow-through experiment, exhibited no indication whatsoever of dichloromethane production.

The destruction of 1,2 DCE and TCE appeared quicker in the flow-through experiments than the batch tests. At first, this seems to be contradictory, in that 1,2 DCE and TCE as single components in the batch tests should intuitively be destructed faster than when in a mixture as in the flow-through experiments. There are several reasons which may shed some light on this occurrence.

1. The mixing action and regime created by the flow-through experiment created increased opportunities for the hydroxyl radicals to attack the VOCs. This would provide

a greater rate of destruction.

2. Although highly unlikely, due to dichloromethane's and benzene's similar rate of destruction to those found in the batch tests, 1,2 DCE and TCE may have volatilized out of the system at some point.

3. The most likely reason for the higher rate of destruction lies within the system design itself. As the solution is passed through the reactor from cylinder to cylinder there is a residence time which the solution spends in one of the cylinders as the other is emptied through the reactor. Reactions are still occurring during this residence time as the unreacted hydroxyl radicals attack the VOCs.

Overall, dichloromethane exhibited more resistance to destruction than the other three VOCs. This was also noted in recent literature. Dichloromethane is the most stable compound of the four VOCs found to contaminate the groundwater at Anniston Army Depot. The carbon, carbon double bonds found in 1,2 DCE and TCE are readily broken as are those found in the benzene ring. It is the inherent structure of the dichloromethane molecule which makes it more difficult to oxidize. In this fact alone the slower rate of destruction for dichloromethane is accounted for.

5 Conclusion

1. It was found that 1,2 dichloroethene, trichloroethene and benzene were readily and rapidly destructed by this advanced oxidation process.

2. Dichloromethane was the time limiting compound for this process. Although it was destructed, it required a much longer time period to achieve desired levels of destruction.

3. The use of a quartz glass reactor significantly enhanced the destruction of VOCs.

4. The bench scale results of this thesis indicate that the UV/H_2O_2 oxidation process is applicable to the contamination found at Anniston Army Depot. Thus the destruction of volatile organic compounds through the use of ultraviolet light and hydrogen peroxide is a very promising alternative in military base remediation efforts and requires much more research.

The next step in this research shall be to obtain actual groundwater samples from Anniston Army Depot. The samples should be treated under the same conditions as found in this thesis. System destruction efficiency for the target compounds will vary due to the other factors associated with groundwater (ie., pH, hardness, turbidity). Here is where all of the parameters which were not varied, must be evaluated to get the required levels of destruction of the target compounds.

6 Recommendations

1. An in-depth study of the hydraulics of the thin film reactor system, perhaps a tracer study, should be conducted. This will help to determine the amount of VOC destruction outside of the reactor.

2. A new system that still uses a thin film reactor, however, on a larger scale should be developed. It should be a continuous closed system, not with two cylinders as it is presently designed with.

3. Obtain a different UV light radiation source in an attempt to vary the range of UV output and determine if the dichloromethane will react differently.

4. Obtain the actual contaminated groundwater and run it through the reactor to evaluate other effects such as pH, turbidity and dissolved solids on the rates of destruction.

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Appendix A

Experimental Results

Flow-through Test - Experiment 1

Time min.	1,2 DCE conc. (ppb)	% remain.	TCE conc. (ppb)	% remain.	Dichloro-methane conc. (ppb)	% remain.	Benzene conc. (ppb)	% remain
0.00	6401.0	100.00	3682.0	100.00	750.8	100.00	45.3	100.00
1.44	4404.0	68.80	2680.0	72.79	906.9	120.79	25.2	55.63
1.80	5088.0	79.49	2403.0	65.26	1258.0	167.55	22.0	48.57
2.16	3855.0	60.22	2367.0	64.29	1146.0	152.64	22.8	50.33
2.52	3758.0	58.71	1739.0	47.23	1263.0	168.22	13.2	29.14
2.88	3596.0	56.18	1892.0	51.39	1350.0	179.81	18.7	41.28
3.60	2024.0	31.62	1623.0	44.08	955.9	127.32	9.8	21.63
5.40	1145.0	17.89	790.0	21.46	1325.0	176.48	nd	0.00
7.20	411.4	6.43	348.0	9.45	1207.0	160.76	nd	0.00
9.00	75.5	1.18	135.5	3.68	934.5	124.47	nd	0.00

Flow-through Test - Experiment 2

Time min.	1,2 DCE conc. (ppb)	% remain	TCE conc. (ppb)	% remain	Dichloro-methane conc. (ppb)	% remain	Benzene conc. (ppb)	% remain
0.00	6589.0	100.00	3463.0	100.00	1095.0	100.00	106.8	100.00
0.93	6653.0	100.97	3011.0	86.95	1176.0	107.40	90.01	84.28
1.55	6511.0	98.82	2677.0	77.30	1450.0	132.42	72.29	67.69
2.16	4505.0	68.37	2145.0	61.94	1165.0	106.39	56.09	52.52
2.78	3765.0	57.14	1889.0	54.55	1071.0	97.81	48.62	45.52
3.40	2975.0	45.15	1923.0	55.53	991.4	90.54	45.56	42.66
4.64	2038.0	30.93	1252.0	36.15	1009.0	92.15	23.69	22.18
6.18	1524.0	23.13	1058.0	30.55	968.8	88.47	14.61	13.68
7.73	923.3	14.01	903.4	26.09	1123.0	102.56	10.14	9.49
9.27	596.1	9.05	485.2	14.01	912.6	83.34	7.82	7.32
10.82	329.4	4.99	369.4	10.67	1107.0	101.10	nd	0.00

Flow-through Test - Experiment 3

Time min.	1,2 DCE conc. (ppb)	1,2 DCE % remain	TCE conc. (ppb)	TCE % remain	Dichloro-methane conc. (ppb)	Dichloro-methane % remain	Benzene conc. (ppb)	Benzene % remain
0.00	4649.0	100.00	1820.0	100.00	709.4	100.00	114.2	100.0
1.17	3331.0	71.65	1452.0	79.78	577.6	81.42	71.5	62.61
2.34	2267.0	48.76	1119.0	61.48	523.9	73.85	42.9	37.57
3.51	1912.0	41.13	934.9	51.37	638.8	90.05	28.3	24.78
5.38	986.2	21.21	607.3	33.37	529.2	74.60	11.6	10.16
7.49	427.3	9.19	313.5	17.23	564.5	79.57	8.6	7.53
9.82	114.6	2.47	107.9	5.93	513.8	72.43	nd	0.0
11.46	34.18	0.74	47.65	2.62	553.2	77.98	nd	0.0
15.20	0.48	0.01	8.02	0.44	506.8	71.44	nd	0.0
18.95	nd	0.0	nd	0.0	408.9	57.64	nd	0.0

Batch Test - 1,2 DCE

Time (min.)	Conc. (ppb)	% Remaining
0.0	6335.00	100.00
1.5	2779.00	43.87
3.0	957.00	15.11
4.5	729.00	11.51
7.0	84.41	1.33
10.0	26.32	0.42
12.5	37.47	0.59
15.0	36.78	0.58
20.0	11.24	0.18
25.0	11.75	0.19

Batch Test - TCE

Time (min.)	Conc. (ppb)	% Remaining
0.0	2577.00	100.00
1.5	260.70	10.12
3.0	141.30	5.48
4.5	38.80	1.51
7.0	65.62	2.55
10.0	26.24	1.02
12.5	19.49	0.76
15.0	56.91	2.21
20.0	31.04	1.20
25.0	29.00	0.97

Batch Test - Dichloromethane

Time min.	Conc. (ppb)	% Remaining
0.0	1877.00	100.00
1.5	1785.00	95.10
3.0	1626.00	86.63
4.5	1041.00	55.46
7.0	1068.00	56.90
10.0	938.50	50.00
12.5	702.10	37.41
15.0	753.00	40.12
20.0	528.40	28.15
25.0	350.00	18.65

Batch Test - Benzene

Time (min.)	Conc. (ppb)	% Remaining
0.0	919.40	100.00
1.5	65.52	7.13
3.0	31.32	3.41
4.5	15.18	1.65
7.0	6.94	0.75
10.0	nd	0.0
12.5	7.24	0.79
15.0	nd	0.0
20.0	6.94	0.75
25.0	7.31	0.80

Batch Test - Mixture of Four VOCs

Time min.	1,2 DCE conc. (ppb)	% remain	TCE conc. (ppb)	% remain	Dichloro-methane conc. (ppb)	% remain	Benzene conc. (ppb)	% remain
0.0	4431.0	100.00	2035.0	100.00	714.1	100.00	78.36	100.00
1.5	2226.0	50.24	1189.0	58.43	705.7	98.82	33.40	42.62
3.0	2021.0	45.61	1177.0	57.84	783.6	109.73	25.25	32.22
4.5	1111.0	25.07	662.8	32.57	669.1	93.70	13.64	17.41
7.0	669.0	15.10	419.2	20.60	704.4	98.64	10.84	13.83
10.0	235.0	5.30	152.2	7.48	585.2	81.95	8.33	10.63
12.5	172.3	3.89	106.1	5.21	626.7	87.76	7.93	10.12
15.0	119.0	2.69	70.8	3.48	397.1	55.61	7.07	9.02
20.0	7.6	0.17	20.5	1.01	254.2	35.60	nd	0.0
25.0	1.4	0.03	11.2	0.55	138.0	19.33	6.98	8.91

Appendix B

Quality Assurance

To maintain the required data quality throughout the experimental period, certain procedures were followed.

1. Glassware Cleanliness

   • Upon completion, or before a set of experiments, all the glassware was rinsed with deionized water, washed with standard lab detergent, rinsed with a 10% HCl solution, rinsed with Super Q water and then placed in the glassware oven for a minimum of two hours at a temperature of 250°C.

2. Thin Film Reactor

   • Upon completion of each experiment, four liters of Super Q water was flushed through the reactor setup. This ensured that any residual VOCs were flushed out of the teflon lines, fittings, the teflon pump and the thin film reactor itself.

3. Sample Storage

   • All samples were stored in clean 15 ml headspace free vials in the original vial storage boxes. They were kept at room temperature until analysis with the GC/MS. Keeping the samples in the covered boxes protected the samples from any incidental UV light radiation. This maintained integrity.

4. GC/MS

   • In order to maintain consistent sample analysis for each analysis, all samples were purged in vial number eight on the purge and trap unit.

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• The vials were rinsed after each purge three times
with Super Q water.

• The mass spectrometer was tuned on a daily basis, or
every 12 hours if in constant use for a period greater
than 12 hours. This was performed using the AUTOTUNE
program within the ChemStation unit.

As an external check on the GC/MS performance used in
this research, one sample from a flow-through experiment was
analyzed at an outside lab. The samples were representative of
the four VOC mixture taken directly from the modified
graduated cylinder before the addition of hydrogen peroxide.

<u>Comparison of GC/MS Results</u>

	U.C.Lab (ppb)	Outside Lab (ppb)	percentage difference
1,2 DCE	3794.0	3908.13	2.92
TCE	1659.0	1980.57	16.24
Dichloro- methane	558.3	986.31	43.39
Benzene	87.15	88.38	1.39

Variability was noted in replicate samples taken during
experimentation. The following lists the concentrations found
present in samples taken at the same time during the flow-
through series of experiments.

Flow-through #3 - Original Sample, no treatment (in ppb).

	Sample 1	Sample 2
1,2 DCE	4464.0	3794.0
TCE	1702.0	1659.0
Dichloromethane	714.0	558.3
Benzene	85.85	87.15

Flow-through #2 - Original Sample, no treatment (in ppb).

	Sample 1	Sample 2
1,2 DCE	6626.0	6557.0
TCE	3737.0	2384.0
Dichloromethane	1274.0	893.8
Benzene	104.9	102.2

Flow-through #2 - Sample after 4.64 min. of treatment (ppb).

	Sample 1	Sample 2
1,2 DCE	3237.0	2038.0
TCE	1285.0	1252.0
Dichloromethane	1383.0	1009.0
Benzene	28.37	23.69

Flow-through #1 - Original Sample, no treatment (in ppb).

	Sample 1	Sample 2
1,2 DCE	5627.0	8017.0
TCE	3750.0	4062.0
Dichloromethane	857.5	886.6
Benzene	54.7	51.44

Flow-through #1 - Sample after 2.16 min. of treatment (ppb).

	Sample 1	Sample 2
1,2 DCE	3113.0	4597.0
TCE	2376.0	2359.0
Dichloromethane	987.5	1305.0
Benzene	17.9	27.86

These apparent differences, some more pronounced than others, are attributable to several causes.

• The actual amount of internal standard injected into samples analyzed may have been different. This would

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adversely effect VOC quantitation.

• The samples were analyzed at different times, sometimes on the order of several days. Unreacted radicals within sample vials may account for the differences in measured concentrations, due to the continued destruct͏ in the samples until analysis.

• Inherent differences within the system itself as it was operated from day to day.

• Contaminants within the lab (especially dichloro-methane), may have contributed to differences in the measured concentrations.

Appendix C

Flow-through Experiment 3 Data

It was noted in the discussion section that reactions were probably taking place outside of the reactor in the cylinder that held the solution which was passed through the reactor. Here, unreacted hydroxyls continued the destruction of the organics present. The following is a list of the times it took to pass the synthetic wastewater solution back and forth through the reactor. All times are in minutes. Under the "samples taken" column the number of samples and time into the pass is noted.

Pass	Time	Cumulative Time	Contact Time	Samples Taken
1	3:54			
2	3:34	7:28		
3	3:50	11:18		
4	3:22	14:40		
5	3:47	18:27	1.17	2 ea., 1:15, 2:00
6	3:12	21:39		
7	3:47	25:26		
8	3:10	28:36		
9	3:37	32:13		
10	3:37	35:50	2.34	2 ea., 1:30, 2:15
11	3:08	38:58		
12	3:33	42:31		
13	3:03	45:34		
14	3:30	49:04		
15	3:25	52:29	3.51	2 ea., 1:30, 2:15
16	2:55	55:24		
17	3:22	58:46		
18	2:58	61:44		
19	3:33	65:17		
20	2:55	68:12		
21	3:22	71:34		
22	2:55	74:29		
23	3:30	77:59	5.38	2 ea., 1:30, 2:15
24	2:53	80:52		
25	3:19	84:10		
26	2:53	87:03		
27	3:13	90:16		

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28	2:54	93:10		
29	3:09	96:19		
30	2:46	99:05		
31	3:11	102:16		
32	3:13	105:29	7 49	2 ea., 1:30, 2:15
33	2:46	108:15		
34	3:05	111:20		
35	2:43	114:03		
36	3:10	117:13		
37	2:49	120:02		
38	3:04	123:06		
39	2:41	125:47		
40	3:02	128:49		
41	2:42	131:31		
42	3:06	134:37	9.62	2 ea., 1:30, 2:00
43	2:38	137:15		
44	3:02	140:17		
45	2:40	142:57		
46	2:59	145:56		
47	2:39	148:35		
48	3:01	151:36		
49	2:54	154:30	11.46	2 ea., 1:30, 2:00
50	2:33	157:03		
51	2:52	159:55		
52	2:30	162:25		
53	2:49	165:14		
54	2:29	167:43		
55	2:55	170:38		
56	2:29	173:07		
57	2:47	175:54		
58	2:29	178:23		
59	2:46	181:09		
60	2:28	183:37		
61	2:50	186:27		
62	2:31	188:58		
63	2:49	191:47		
64	2:30	194:17		
65	2:48	197:05	15.70	2 ea., 1:30, 2:00
66	2:29	199:34		
67	2:45	202:19		
68	2:25	204:44		
69	2:43	207:27		
70	2:23	209:50		
71	2:37	212:27		
72	2:22	214:49		
73	2:38	217:27		
74	2:22	219:49		

75	2:39	222:28		
76	2:22	224:50		
77	2:50	227:40		
78	2:21	230:01		
79	2:43	232:44		
80	2:23	235:07		
81	2:00	237:07	18.95	2 ea., 1:30, 2:00